J. Phys. Chem. A **2002,** *106,* 2721−2726

Valence Bond Configuration Interaction: A Practical ab Initio Valence Bond Method That Incorporates Dynamic Correlation

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Received: November 9, 2001; In Final Form: December 28, 2001

A post-VBSCF method, called valence bond configuration interaction (VBCI), is developed here. The method incorporates dynamic correlation, by use of configuration interaction (CI) to improve the energetics after a VBSCF calculation. The levels of CI are fashioned as in the corresponding molecular orbital approach. Thus, VBCIS involves only single excitations, while VBCISD involves also doubles, and so on. The VBCI method retains the simplicity of a VB presentation by expressing the wave function in terms of a minimal number of effective structures that dictate the chemistry of the problem. The method was tested by calculating the bond energies of H_2, LiH, HF, HCl, F_2, and Cl_2 as well as the barriers of identity hydrogen abstraction reactions, $X\bullet + X'H \rightarrow XH + X'\bullet$ (X, $X' = CH_3$, SiH_3, GeH_3, SnH_3, or PbH_3). It is shown that VBCIS gives results that are at par with breathing orbital valence bond method. The VBCISD method is better and its results match those of the molecular orbital based coupled cluster CCSD method. Future potential directions of the development of the VBCI approach are outlined.

Introduction

Molecular orbital (MO) theory is the main computational method in contemporary quantum chemistry. Nevertheless, valence bond (VB) theory remains as a widespread conceptual matrix for many chemists. The stumbling block for the development of VB theory has always been its quantitative implementation. Thus, VB methods generally require extensive computation times, while their accuracy is not always satisfactory. To convert VB theory into a mainstream method in contemporary quantum chemistry, one needs to develop practical VB methods that possess accuracy at the lowest possible time consumption. This is the primary goal of the present paper, which introduces a valence bond configuration interaction method.

The classical VB method, which uses covalent and ionic structures based on unoptimized atomic orbitals (AOs), is extremely poor.[1] A considerable improvement is obtained in the VBSCF method,[2] when the orbitals of the classical VB structures are allowed to optimized. The VBSCF method takes care of the static electron correlation and gives equivalent results to CASSCF.[3] A similar quality is exhibited by the generalized VB (GVB)[4] and the single configuration spin coupled VB (SCVB)[5] methods. These methods, however, used semidelocalized orbitals and as such their VB structures do not correspond anymore to the classical structures,[6] except for cases where bond ionicity is not significant. VBSCF lack dynamic correlation, which is very important for obtaining good accuracy.

A VB method which incorporates dynamic correlation is the breathing orbital VB (BOVB)[7] method. This method provides an extra degree of freedom during orbital optimization, such that each VB structure ends up having its own set of orbitals. Thus, the orbitals adopt themselves to the instantaneous field of the VB structures, rather than to the mean field of all the structures,[8] as is the case in VBSCF, GVB or SCVB. This degree of freedom in BOVB introduces dynamic correlation, and thereby improves considerably the accuracy of the results.[1]

One drawback of the BOVB method is its time consumption and its occasional failure to converge when many VB structures are used.[1] While most of these difficulties can be overcome by expert users.[1,9] This creates difficulties for general users who are not VB experts. A logical step forward is to devise a method that keeps the conceptual clarity of the classical VBSCF method, while incorporating dynamic correlation like BOVB, but in a manner that is less time-consuming. Approaches that include dynamic correlation in VB theory have been proposal already by Hiberty et al,[10] Gallup et al,[11] Nascimento et al.,[12] Wu and McWeeny,[13] Cooper et al.,[14] and so on. Thus, Hiberty et al.[10] have shown that if the classical VB structures are augmented by configuration interaction, using single excitations, the quantitative accuracy is greatly improved. In fact, the use of single excitations is approximately equivalent to a BOVB procedure performed with a minimal number of structures. The present paper follows these ideas and introduces a general method that augments a VBSCF calculation by subsequent configuration interaction (CI), or in short VBCI. The paper describes the formulation of the virtual space of orbitals, outlines the CI methodology and the condensation of the final CI space into a minimal number of VB structures dictated by the chemical problem. The paper then follows with some applications to the calculations of bond energies and reaction barriers. As shall be demonstrated, the VBCI method is quantitatively equivalent to the MO−Based CCSD method and to the BOVB method, when

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10.1021/jp0141272 CCC: $22.00

all are performed at the same conditions; basis set and number of optimized orbitals.

Theory and Methodology

A. The Spin-Free Approach for Valence Bond Theory. The VB calculations use the spin-free formulation of quantum chemistry. The spin-free approach for VB theory has been fully described elsewhere[15−17] and will be sketched only briefly.

In spin-free VB theory, a many-electron wave function is expressed in terms of spin-free VB functions Φ_K,

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

Φ_K may be a bonded tableau (BT) state,[16] defined as

$$\Phi_K = N_K e_{r1}^{[\lambda]} \Omega_K \tag{2}$$

where N_K is a normalization factor, $e_{rs}^{[\lambda]}$ is a standard projector of the symmetric group S_N, defined through the irreducible representation matrix elements, $D_{rs}^{[\lambda]}(P)$, as

$$e_{rs}^{[\lambda]} = \left(\frac{f_\lambda}{N!}\right)^{1/2} \sum_{P\in S_N} D_{rs}^{[\lambda]}(P)P \tag{3}$$

where f_λ is the dimension of the irreducible representation $[\lambda]$, and Ω_K is an orbital product,

$$\Omega_K = \phi_{k_1}(1)\phi_{k_2}(2)\phi_{k_3}(3)\phi_{k_4}(4)...\phi_{k_N}(N) \tag{4}$$

which maintains a one by one correspondence with the usual VB structure, by the arrangement of orbital indices.

With this permutation symmetry-adapted basis eq 2, the Hamiltonian and overlap matrix elements are written respectively as

$$H_{KL} = \langle \Phi_K | H | \Phi_L \rangle = \sum_{P\in S_N} D_{11}^{[\lambda]}(P) \langle \Omega_K | HP | \Omega_L \rangle \tag{5}$$

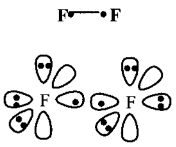
and

$$M_{KL} = \langle \Phi_K | \Phi_L \rangle = \sum_{P\in S_N} D_{11}^{[\lambda]}(P) \langle \Omega_K | P | \Omega_L \rangle \tag{6}$$

The coefficients C_K in eq 1 are subsequently determined by solving the usual secular equation $\mathbf{HC} = E\mathbf{MC}$.

The so-called "N!" difficulty is that the Hamiltonian and overlap matrix elements, eqs 5 and 6, contain N! terms due to the use of nonorthogonal orbitals. To ameliorate this problem, Wu et al.[17] developed recently the paired-permanent-determinant approach using symmetric group techniques. This approach is implemented in an ab initio VB program, XIAMEN-99 package,[18] with which all the calculations are performed.

B. Virtual VB Orbitals and Excited VB Structures. One of the most important advantages of VB theory is that it can provide insight into chemical problems even with only a few VB structures. In the VBSCF method, only structures that are essential for the description of the particular chemical problem are involved in calculation. The orbitals and coefficients of the VB structures are optimized simultaneously to minimize the total energy. In the present work, the structures that are used in the VBSCF calculation are referred to as fundamental structures, denoted as Φ_K^0, and the VB orbitals that appear in the VBSCF structures are referred to as occupied VB orbitals. For example, in the F_2 case as a prototypical bond energy problem, one covalent and two ionic structures are used for the VBSCF wave function. By freezing the 1s orbitals, there remain eight occupied VB orbitals (six lone pairs and two bonding orbitals) that are described in **1**−**3**. Thus, all the valence orbitals are referred to as occupied VB orbitals, and are optimized during the calculation.



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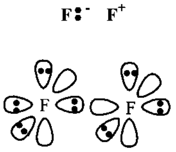

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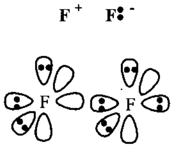


3

A VB orbital is usually written as a linear combination of basis functions,

$$\phi_i = \sum_{\alpha=1}^{m} c_{\alpha i}\chi_\alpha, \quad i = 1, 2, ..., n \tag{7}$$

where the coefficients are optimized in the VBSCF calculation. The form of the expression depends on whether localized, delocalized, or bond-distorted orbitals[8c] are required for the particular application. In the present work, the basis functions are grouped into different blocks

$$\{\chi_\alpha\} = \{\chi_1^A, \chi_2^A, ..., \chi_{m_A}^A; \chi_1^B, \chi_2^B, ..., \chi_{m_B}^B; \chi_1^C, \chi_2^C ..., \chi_{m_C}^C; ...) \tag{8}$$

where the superscripts A, B, and C of χ stand for blocks A, B, and C, respectively. The blocks can be defined by reference to the whole molecules, or its fragments, atoms, etc. If delocalized orbitals (Coulson−Fischer orbitals[19]) are used, there will be only one block, which covers the entire system. The occupied VB orbitals in a given block are expanded over the basis set which belongs to that block. For example, ϕ_i^A, which belongs to block A, will be written as follows:

$$\phi_i^A = \sum_{\alpha=1}^{m_A} c_{\alpha i}^A \chi_\alpha^A \tag{9}$$

Taking again F_2 as an example, suppose we wish to do a calculation with localized VB orbitals. One can then divide the basis functions into four blocks: σ-type basis functions centered on F_1, σ-type basis functions centered on F_2, π-type basis functions centered on F_1, and π-type basis functions centered on F_2. Scheme 1 shows the four blocks for 6-31G basis set.

In a traditional VBSCF method, only occupied VB orbitals are optimized in the calculation and it is not essential to define virtual VB orbitals. However, virtual orbitals are required if one wishes to adapt a configuration interaction technique in the VB method. To keep the advantage of classical VB theory, the virtual VB orbitals should also be strictly localized, much like the occupied VB orbitals. In the present work, virtual VB orbitals are defined over the various blocks,

$$\phi_a^A = \sum_\beta c_{\beta a}^A \chi_\beta^A \tag{10}$$

Obviously, the total number of occupied and virtual VB orbitals for block A should be the same as the number of the basis

SCHEME 1

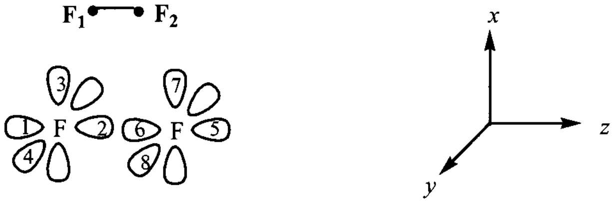
Block *A*: $2s(1)$, $2s'(1)$, $2p_z(1)$, $2p_z'(1)$

Block *B*: $2p_x(1)$, $2p_x'(1)$, $2p_y(1)$, $2p_y'(1)$

Block *C*: $2s(2)$, $2s'(2)$, $2p_z(2)$, $2p_z'(2)$

Block *D*: $2p_x(2)$, $2p_x'(2)$, $2p_y(2)$, $2p_y'(2)$

SCHEME 2



	$2s(1)$	$2s'(1)$	$2p_z(1)$	$2p_z'(1)$
Occupied				
1:	0.5276	0.5380	-0.0428	-0.0300
2:	0.0228	-0.0316	0.7095	0.4339
Virtual				
1':	-1.4277	1.4251	-0.0194	-0.0018
2':	0.0090	-0.0118	-0.9108	1.0701

	$2p_x(1)$	$2p_x'(1)$	$2p_y(1)$	$2p_y'(1)$
Occupied				
3:	0.6865	0.4610	0.0000	0.0000
4:	0.0000	0.0000	0.6865	0.4610
Virtual				
3':	0.9280	-1.0582	0.0000	0.0000
4':	0.0000	0.0000	0.9280	-1.0582

functions in block A. Thus, the total number of occupied and virtual VB orbitals for the entire molecule is equal to the total number of basis functions.

A way to define the virtual orbitals of block A is to use a projector[20]

$$\mathbf{P}_A = \mathbf{V}_A(\mathbf{M}_A)^{-1}\mathbf{V}_A{}^{+}\mathbf{S}_A \tag{11}$$

where $\mathbf{V}_A$ is the vector of orbital coefficients. The $\mathbf{M}_A$ and $\mathbf{S}_A$ are the overlap matrixes of the occupied VB orbitals and the basis functions, respectively, while the index A indicates that all matrixes are associated with block A. It can be shown that the eigenvalues of the projector $\mathbf{P}_A$ are 1 and 0. The eigenvectors associated with eigenvalue 1 are the occupied VB orbitals, while the eigenvectors associated with the eigenvalue 0 are used as the virtual VB orbitals of block A. The virtual VB orbitals produced in this manner share two important features. They are strictly localized on block A and are at the same time orthogonal to the occupied VB orbitals $\{\phi_i^A\}$. By diagonalizing the projectors for all blocks, we can have all the virtual VB orbitals, which belong to different blocks. In the case of F_2 with 6-31G, there are eight virtual orbitals, which are distributed in the four blocks, defined in Scheme 1. As an example, we give in Scheme 2 the symmetry unique VB and virtual orbitals of an atom F in the F_2 molecule, using the 6-31G basis set.

After generating the virtual VB orbitals, we can create excited VB structures in the following way: Given a fundamental VB structure Φ_K^0, an excited VB structure Φ_K^i is built by replacing occupied VB orbital(s) ϕ_i^A with virtual orbital(s) ϕ_a^A. By restricting the replacement of virtual orbital ϕ_a^A to the same block as ϕ_i^A, the excited VB structure Φ_K^i retains the same electronic pairing pattern and charge distribution as Φ_K^0. In other words, both Φ_K^i and Φ_K^0 describe the same "classical" VB structure. Thus, the collection of excited VB structures nascent from a given fundamental structure serve to relax the fundamental VB structure and endow it with instantaneous dynamic correlation. Since all the fundamental structures experience simultaneously the same effect, the end result is like a set of fundamental VB structures which are internally correlated and adopted to mix with each other, to yield the lowest possible energy within the particular type of the wave function.

C. Valence Bond Configuration Interaction (VBCI) Method. Once a VBSCF calculation involving all the fundamental VB structures is carried out, as in eq 12,

$$\Psi^{\mathrm{VBSCF}} = \sum_K C_K^{\mathrm{SCF}}\,\Phi_K^0 \tag{12}$$

and the occupied VB orbitals are optimized, the virtual orbitals and the excited VB structures are automatically created. A subsequent VBCI calculation will involve all the fundamental and the excited VB structures,

$$\Psi^{VBCI} = \sum_K \sum_i C_{Ki}\Phi_K^i \tag{13}$$

where the coefficients C_{Ki} are determined by solving the secular equation without further orbital optimization. The total energy of the system is

$$E^{\mathrm{VBCI}} = \frac{\sum_{K,L}\sum_{i,j} C_{Ki}C_{Lj}\langle\Phi_K^i|H|\Phi_L^j\rangle}{\sum_{K,L}\sum_{i,j} C_{Ki}C_{Lj}\langle\Phi_K^i|\Phi_L^j\rangle} \tag{14}$$

Since the CI space is large, we can truncate this space following the usual CI methodology. The starting point always involves single excitations, i.e., VBCIS. This can be followed by VBCISD, VBCISDT, etc., where D stands for double and T for triple excitations. The level at which truncation is employed will depend on the size of the problem and the desired accuracy. *However, what is important is the fact that the results can be improved systematically.*

One of the most important advantages of modern VB theory is that it provides chemical insight with a very compact wave function. The VBCI method has this feature since it enable one to represent the CI wave function, eq 13, in a compact form,

$$\Psi^{\mathrm{VBCI}} = \sum_K C_K^{\mathrm{CI}}\,\Phi_K^{\mathrm{CI}} \tag{15}$$

where VB structure Φ_K^{CI} is of the form in eq 16,

$$\Phi_K^{CI} = \sum_i C'_{Ki}\Phi_K^i \tag{16}$$

which collects all the VB functions that belong to the same structure in terms of pairing and charge distribution.

The coefficients C_K^{CI} and C'_{Ki} is determined by the normalization of Φ_K^{CI}, written respectively as

$$C_K^{\mathrm{CI}} = (\sum_{i,j} C_{Ki}C_{Kj}\langle\Phi_K^i|\Phi_K^j\rangle)^{-1/2} \tag{17}$$

and

$$C'_{Ki} = C_{Ki}/C_K^{\mathrm{CI}} \tag{18}$$

The elements of the compact Hamiltonian and overlap matrixes are respectively written as

$$H_{KL}^{\mathrm{CI}} = \sum_{i,j} C_{Ki}C_{Lj}\langle\Phi_K^i|H|\Phi_L^j\rangle \tag{19}$$

and

$$M_{KL}^{\mathrm{CI}} = \sum_{i,j} C_{Ki}C_{Lj}\langle\Phi_K^i|\Phi_L^j\rangle \tag{20}$$

Structural weight analysis is one of the most important advantages of VB theory. The weight of an individual VB structure given by

$$W_{Ki} = \sum_{L,j} C_{Ki}\langle\Phi_K^i|\Phi_L^j\rangle C_{Lj} \tag{21}$$

is not so important by itself. What is more important is the total weight of the fundamental and its excited structures that belong to the same electronic structure. Thus, the combined weight is summed over all these structures to give a weight of a single VB structure.

$$W_K = \sum_i W_{Ki} \tag{22}$$

In this manner, the extensive VBCI wave function is condensed to a minimal set of fundamental structures that are all dressed with dynamic correlation.

D. The Structure of the Hamiltonian and Overlap Matrixes. It is well-known that the Hamiltonian and overlap matrixes in the MO-based CI are sparse due to orthogonal molecular orbitals. Unfortunately, for the VBCI method, these two matrixes are not sparse because of the use of nonorthogonal VB orbitals. However, we can still obtain the following properties of the Hamiltonian and overlap matrixes.

Property 1. A Hamiltonian matrix element H_{KL} is zero if there are three VB orbitals in Φ_K (Φ_L) that are orthogonal to all VB orbitals in Φ_L (Φ_K).

Property 2. An overlap matrix element M_{KL} is zero if there is one VB orbital in Φ_K (Φ_L) that is orthogonal to all VB orbitals in Φ_L (Φ_K).

With properties 1 and 2, we can determine if a given matrix element is zero or not without computing. From the applications tried so far, about 20% of the matrix elements are zero.

Applications

All the calculations were performed with the Xiamen VB package[18] that incorporates the VBCI method.

A. Bond Energies. The VBCIS and VBCISD are applied to the bond energy calculations of diatomic molecules: H_2, LiH, HF, HCl, F_2, and Cl_2. The Pople basis set 6-31G** is used in the calculations, and the geometries are optimized by CCSD/6-31G**. All electrons in the inner shells are frozen at their Hartree−Fock level. Three fundamental VB structures, one covalent and two ionic structures, as shown in Scheme 3, are used for the VBSCF calculations. For H_2 and LiH, basis functions on each atom form a block. Thus, there are two blocks for these two molecules. For the other molecules, e.g., F_2, σ-π separation is used, and there result four blocks.

Table 1 shows the VBCI bond energies of the molecules with various methods. It can be seen that the Hartree−Fock bond energies are poor as expected. The simple VBSCF bond energies are much improved, but still not quantitatively good, especially for F_2 and Cl_2, which are known to be difficult cases for bond energy calculations. VBCIS provides already good bond energies similar to the D-BOVB method.[7] The VBCISD bond energies are even better and in very good agreement with those of CCSD. The number of the VB structures involved in the VBCI calculations, as shown in Table 1, is very small compared to the number of the configurations that are involved in the molecular orbital based CI. This is due to the fact that the VB excitations are restricted within blocks.

Table 2 shows the weights of one covalent and two ionic structures for all the molecules. It can be seen that the weights for various methods are in very good agreement. The weights of the covalent structures for VBCIS and VBCISD are slightly lower than those of VBSCF, and are similar to the BOVB weights.

B. Reaction Barriers. As a second application of the VBCI method, we calculated the barriers of identity hydrogen abstraction reactions,[22] X• + X′H → XH + X′• (X, X′ = CH_3, SiH_3, GeH_3, SnH_3, or PbH_3). The Pople basis set 6-31G* is used for X = CH_3 and SiH_3 and LANL2DZ/31G* for the rest. All geometries are optimized at the MP2 level. Eight structures, as shown in Scheme 4, are involved in the calculations.

Table 3 shows the resulting barriers for various methods. With exception of entries 2 and 8, all the electrons in the inner shell

TABLE 1: Bond Energies (D) with Various Methods (kcal/mol)

molecule	D^{HF}	D^{B3LYP}	D^{CCSD}	D^{VBSCF}	$D^{BOVB\ a}$	$D^{VBCIS\ b}$	D^{VBCISD}	$D^{exptl\ c}$
H_2	84.6	111.7	105.9	95.8	96.0	96.0(11)	105.9(55)	104.2
LiH	32.5	57.2	49.5	42.4	43.0	42.8(27)	49.6(118)	56.6
HF	94.9	132.4	127.2	105.1	115.9	125.0(40)	126.0(274)	137.2
HCl	77.6	103.1	99.1	85.8	89.9	92.0(40)	98.0(274)	101.2
F_2	−33.1	41.4	28.3	10.9	31.5	40.4(81)	33.9(1089)	38.0
Cl_2	14.5	48.4	41.6	26.2	35.6	38.9(81)	42.1(1089)	58.0

[a] The BOVB method refers to D-BOVB described in ref 1. Much better results are obtained with SD-BOVB, which splits the filled orbitals of the ionic structures. [b] Values in parentheses are the number of VB structures involved in the calculations. [c] All experimental values are from ref 21.

SCHEME 3

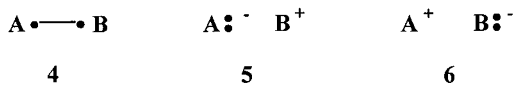
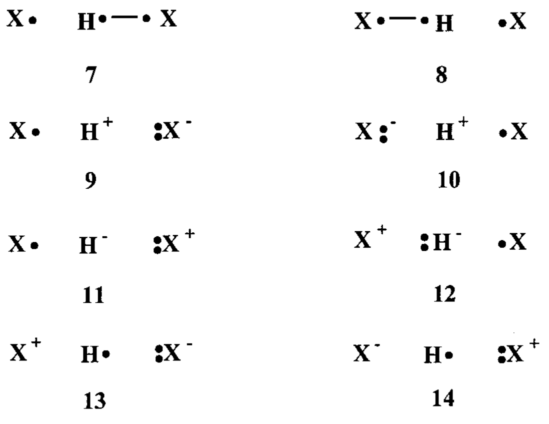


TABLE 2: Weights of the VB Structures 4−6 (See Scheme 3) for Various VB Methods

	H_2	LiH	HF	HCl	F_2	Cl_2
VBSCF						
covalent	0.8074	0.8919	0.5829	0.6708	0.7933	0.6949
ionic	0.0963	0.0028	0.0106	0.0725	0.1033	0.1531
	0.0963	0.1053	0.4066	0.2567	0.1033	0.1520
BOVB[a]						
covalent	0.7606	0.8756	0.5182	0.6486	0.7012	0.6513
ionic	0.1197	−0.0062	0.0637	0.0998	0.1494	0.1744
	0.1197	0.1306	0.4181	0.2516	0.1494	0.1744
VBCIS						
covalent	0.7489	0.7622	0.5024	0.6386	0.6975	0.6439
ionic	0.1256	0.0520	0.0530	0.1022	0.1513	0.1781
	0.1256	0.1858	0.4446	0.2593	0.1513	0.1780
VBCISD						
covalent	0.7727	0.8799	0.5515	0.6547	0.7395	0.6637
ionic	0.1137	−0.0137	0.0191	0.0847	0.1305	0.1681
	0.1137	0.1338	0.4293	0.2606	0.1300	0.1682

[a] This refers to D-BOVB (See ref 1).

SCHEME 4



and eight π electrons are frozen at their Hartree−Fock form. In entries 2 and 8 all orbitals are optimized. It is seen that the VBCIS barriers (entry 6) are slightly less good than those of D-BOVB (entry 5), while VBCISD results (entry 7) compatible with the D-BOVB data (entry 5). The VBCISD results are at par with CCSD values that are obtained by freezing the π orbitals during the CCSD procedure (entry 3). At present, performing VBCISD with excitation from all valence electron is too time-consuming due to the size of the CI. This size is determined not only by the atomic basis set, but also by the number of fundamental structures, which for this problem is eight (Scheme 4). A VBCIS calculation involving all the valence electrons (entry 8) gives good agreement with those of CCSD (entry 2) for X =CH_3 and SiH_3, but not for X = GeH_3, SnH_3, and PbH_3. Apparently, the use of effective core potential (LANL2DZ) requires a higher level of excitation than singles only.

TABLE 3: The Barriers of X• + X′H → XH + X′• (X = CH_3, SiH_3, GeH_3, SnH_3, or PbH_3) (kcal/mol)

entry	method	CH_3	SiH_3	GeH_3	SnH_3	PbH_3
1	HF	35.1	25.2	22.0	18.5	15.2
2	CCSD[a]	22.5	15.7	12.8	10.7	8.2
3	CCSD[b]	26.5	19.3	16.6	13.5	13.0
4	VBSCF[b]	33.0	25.9	25.5	20.5	17.3
5	BOVB[b]	23.1	19.1	18.0	14.9	12.3
6	VBCIS[b]	26.7	19.2	18.9	15.5	12.7
7	VBCISD[b]	24.5	17.9	17.5	14.8	11.4
8	VBCIS[a]	22.7	17.5	17.3	14.2	11.5
9	Exp.	14.7[c](18)[d]				

[a] No valence orbitals are frozen. [b] All orbitals with π symmetry with respect to the X−H-X axis are held frozen. [c] Activation energy from ref 23. [d] Barrier estimated from the activation energy in (c). See ref 23.

TABLE 4: Size Consistency in VBCISD and CISD

	ΔE(size)[a]	
method	F_2	C_2H_7[b]
VBCISD	0.6	1.4
CISD[c]	4.4	8.0

[a] ΔE(size) = E(separate fragments) − E(supermolecule with fragments at 10 Å). [b] The two fragments are CH_3 and CH_4. C_2H_7 itself is the transition state for the reaction described in Table 3. [c] This is the molecular orbital based CI.

Size consistency problems exist in all configuration interaction methods whenever a truncation technique is adapted. Obviously, we were also concerned about the problem in the VBCI method. Table 4 shows that the total energy of F_2 at R_{FF} = 10 Å obtained by computing it as a whole molecule and by computing two F atoms, respectively. A similar calculation was carried out for the C_2H_7 transition state from Table 3. In both cases, it can be seen that the problem of size-insistency in VBCI is negligible (0.6−1.4 kcal/mol), in contrast with the MO based CISD method that suffers from a serious inconsistency (4.4−8.0 kcal/mol).

Summary

This paper presents a post-VBSCF method, called VBCI. The method uses configuration interaction technique to improve the energetics after a VBSCF calculation. The levels of CI are fashioned as in the corresponding molecular orbital approach. Thus, VBCIS involves only single excitations, while VBCISD involves also doubles, and so on. From this point of view VBCI has no limitations, *in principle*, since it can always be improved systematically with the increasing computing power and improvements in software. From a conceptual point of view, VBCI retains the simplicity of a VB presentation since the wave function is ultimately expressed in terms of a minimal number of effective structures that dictate the chemistry of the problem.

The tests in this paper show that VBCIS gives results that are at par with D-BOVB. The VBCISD method is somewhat better and its results match those of the molecular orbital based coupled cluster CCSD method. At present, the VBCISD procedure is still time-consuming for problems with many fundamental structures and more than 14 valence electrons as in the problem presented in Table 3. The practical solutions are either to use VBCIS with all valence orbitals or VBCISD with a few frozen valence orbitals. VBCIS can often be a practical economic solution as shown by the example of C_2H_7 in Table 3 (entry 8).

The CPU limitations of VBCI can be overcome in a few manners. Improvement of the paired-permanent-determinant (PPD) approach for the spin-free VB theory[17] can be achieved by making use of the fact that most of sub-PPDs required in the evaluation of a fundamental VB structure are the same as those of its excited VB structures. In addition, ideas of perturbation theory and coupled cluster can be imported into VB theory to generate a family of new and economical post-VBSCF methods. Such methods are under development.

Acknowledgment. The research at XMU is supported by the Natural Science Foundation of China (Grants 20073033 and 20021002). The research at HU is supported in part by the Robert Szold Foundation and the VW Stiftung through the Ministry of Sciences of the Niedersachsen States.

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