Breathing Orbital Valence Bond Method in Diffusion Monte Carlo: C−H Bond Dissociation of Acetylene[†]

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Received: March 6, 2008; Revised Manuscript Received: May 2, 2008

This study explores the use of breathing orbital valence bond (BOVB) trial wave functions for diffusion Monte Carlo (DMC). The approach is applied to the computation of the carbon−hydrogen (C−H) bond dissociation energy (BDE) of acetylene. DMC with BOVB trial wave functions yields a C−H BDE of 132.4 ± 0.9 kcal/mol, which is in excellent accord with the recommended experimental value of 132.8 ± 0.7 kcal/mol. These values are to be compared with DMC results obtained with single determinant trial wave functions, using Hartree−Fock orbitals (137.5 ± 0.5 kcal/mol) and local spin density (LDA) Kohn−Sham orbitals (135.6 ± 0.5 kcal/mol).

1. Introduction

Acetylene (C_2H_2) and the hydrogen-abstracted ethynyl radical (C_2H) are important in interstellar, flame and combustion chemistry. Due to their relatively small size and importance, these molecules have been studied extensively both experimentally and theoretically,[1–7] and therefore can also serve as excellent test cases for gauging the accuracy of a computational approach.

Quantum Monte Carlo (QMC) [8–11] methods present interesting alternatives to basis set ab initio methods.[12,13] In QMC, the trial wave function is typically constructed as the product of a determinantal expansion and a correlation function, the latter containing explicit interparticle distance terms. In diffusion Monte Carlo (DMC), the imaginary time evolution operator is applied to sample a distribution that is a product of the trial wave function and the unknown exact wave function. The DMC method requires that this distribution be positive definite which leads to the imposition of the known nodes of the trial wave function on the exact wave functions.[9–11,14–18] The difference between the DMC predicted total energy and the exact total energy, is solely due to this fixed-node approximation. A consequence of the fixed-node approximation is that DMC prediction of bond dissociation energies (BDEs) can be a difficult task because the fixed-node error of the parent molecule and dissociation fragments should ideally be comparable, as reflected in similar correlation energy recovered, to obtain accurate BDEs.

In a systematic DMC study, Barnett et al.[19] explored the effect of multideterminant trial wave functions, obtained by retaining only the configuration state functions (CSFs) with the largest coefficients from multiconfigurational self-consistent field (MCSCF) calculations, on the total DMC energy. Typically 89−91% of the correlation energy was recovered for C_2H radical while 96−97% of the correlation energy was obtained for C_2H_2. This unbalanced recovery of correlation energy for the two molecules resulted in a large overestimation of the DMC BDE. For both C_2H and C_2H_2, little correlation energy was gained by increasing the trial wave function from a single CSF to several dozen CSFs. Since the computational cost of DMC calculations grows rapidly with number of determinants in the trial wave function, MCSCF expansions rapidly become prohibitive as general trial wave functions for DMC calculations.

An alternative ab initio methodology to molecular orbital (MO)-based methods, such as MCSCF and CI (configuration interaction), are the family of valence bond (VB) methods.[20] The VB methods do not require orthonormality of the orbitals, and VB determinantal expansions can be more compact than those obtained from MCSCF procedures. This feature has the potential of making VB expansions desirable as DMC trial wave functions. Because VB orbitals are generally localized on one or two centers, a VB based trial wave function could be cheaper than a trial wave function of the same expansion length based on MOs delocalized over the entire molecule. A possible advantage of VB trial wave functions is that it is simple to construct compact wave functions that contain nondynamical electron correlation over the course of a dissociation process. Such trial wave functions could give a balanced description of parent and dissociation fragments, and lead to improved DMC BDEs. In this study, we explore the merits of using ab initio VB wave functions for DMC. The only DMC electronic structure studies to date that have used trial wave functions related to VB theory are those of Sorella and co-workers using geminals.[21,22]

In this article we present a follow-up study to the DMC BDE benchmark study of Kollias et al.[23] We explore the use of multideterminantal trial wave functions obtained from breathing orbital valence bond (BOVB) calculations [24,25] as possible systematic improvements on single determinantal trial wave function obtained from Hartree−Fock (HF) and density func-

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[†] Part of the special section for the "Symposium on Energetics and Dynamics of Molecules, Solids and Surfaces".

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10.1021/jp8020062 CCC: $40.75

TABLE 1: Ab Initio Basis-Set Calculation Total Energies[a] (in hartrees) and Acetylene C−H Bond Dissociation Energies (in kcal/mol)

	HF/TZP	p-BOVB/TZP	SD-BOVB/TZP	CCSD(T)/TZP[b]	CCSD(T)/cc-pVQZ[b]	exptl
C_2H	−76.16070	−76.24711	−76.24420	−76.43155	−76.48718	−76.61[c]
	0.0%	19.2%	18.6%	60.3%	72.7%	
C_2H_2	−76.84763	−76.94339	−76.95512	−77.14397	−77.20910	−77.33[c]
	0.0%	19.9%	22.3%	61.4%	74.9%	
BDE[d]	112.1	118.0	127.2	128.2	134.1	132.8(7)[e]

[a] Ab initio basis-set calculations performed at B3LYP/cc-pVTZ geometries followed by estimated percentage of correlation energy recovered. [b] UCCSD(T) was used for C_2H and RCCSD(T) was used for C_2H_2. [c] Estimated exact total energy from ref 19. [d] To calculate the BDE from the ΔE, a thermal-vibration correction of −5.2 kcal/mol is used, see the thermochemistry section. $E(H) = -0.49996$ hartree for HF/TZP, p-BOVB/TZP, SD-BOVB and CCSD(T)/TZP. $E(H) = -0.49995$ hartree for CCSD(T)/cc-pVQZ. [e] Recommended experimental BDE from ref 47.

TABLE 2: DMC Total Energies[a] (in hartrees) and Acetylene C−H Bond Dissociation Energies (in kcal/mol)

	DMC[b]	DMC/1-det[c]	DMC/1-det[d]	DMC/p-BOVB[e]	exptl
C_2H		−76.5843(5)	−76.5889(6)	−76.5889(7)	−76.61[f]
		94.3(1)%	95.3(1)%	95.3(2)%	
C_2H_2		−77.3117(5)	−77.3133(5)	−77.3081(13)	−77.33[f]
		96.2(1)%	96.5(1)%	95.4(3)%	
BDE[g]	136.6(1)	137.5(5)	135.6(5)	132.4(9)	132.8(7)[h]

[a] DMC calculations performed at B3LYP/cc-pVTZ geometries followed by estimated percentage of correlation energy recovered. [b] DMC calculations with HF trial functions from ref 23. Total energies are not reported since the calculations were performed with ECPs. [c] This work using single determinant trial wave functions from HF/TZP. [d] This work using single determinant trial wave functions constructed from LDA/TZP Kohn−Sham orbitals. [e] This work using multideterminant trial wave functions from p-BOVB/TZP calculations. [f] Estimated exact total energy from ref 19. [g] To calculate the BDE from the ΔE, a thermal-vibration correction of −5.2 kcal/mol is used, see thermochemistry section. [h] Recommended experimental BDE from ref 47.

tional theory (DFT) for DMC computations. The advantage of the BOVB method over most other VB methods is that additional correlation is included in the wave function, without additional determinants, due to the flexibility of different orbitals for different VB structures. This flexibility enables active orbitals to respond to instantaneous charge fluctuations that occur during the dissociation process by changing size, polarization and hybridization. In analogy to vibrational breathing modes, these flexible orbitals are called ”breathing orbitals” by Hiberty et al.[25]

In Section II, we outline the computational methodology with focus on DMC trial wave function construction, follow with molecular geometry considerations and conclude the section with relevant thermochemistry. The succeeding section presents the results of the computations followed in Section IV by conclusions.

2. Computational Methodology

2.1. DMC and Trial Wave Function Construction. The DMC method stochastically solves the nonrelativistic time-independent Schrödinger equation by simulating the time-dependent Schrödinger equation in imaginary time. Because the DMC method has been thoroughly described elsewhere (see, for example, refs 14–16, 10, 9, 11, 17, 18) we only give information needed for the present computations.

The Zori quantum Monte Carlo code[26] was used for the present DMC calculations. Trial wave functions were of the form of one or more Slater determinants (obtained from HF, LDA or BOVB) multiplied by a 10-parameter Schmidt−Moskowitz−Boys−Handy (SMBH) correlation function.[27] The latter function contains terms involving explicit electron−electron, electron-nucleus, and electron-other-nucleus distances. The correlation function serves to reduce the variance in the local energy and improve the stability of the DMC calculations. Since the correlation function is positive definite it does not change the nodes of the wave function nor the fixed-node DMC energy. Unlike the Kollias et al. study,[23] we use all-electron polarized triple-ζ Slater basis sets (TZP)[28] of the ADF software package[29–31] for the determinantal part of our wave functions, rather than effective core potentials (ECPs) and Gaussian basis sets. The SMBH correlation function parameters were obtained by minimizing the absolute deviation functional[32,33] of the local energy over a fixed set of 32 000 walkers. Upon the initial equilibration of the 32 000 walkers using the Reynolds et al. algorithm[14] with single electron moves, a series of all-electron-move DMC calculations at 4 time steps were performed with each trial wave function. These calculations were carried out at time steps of 0.0010, 0.000 75, 0.000 50, and 0.000 25 hartree^{-1} using the Umrigar et al. all-electron-move algorithm[15] in conjunction with the DePasquale et al. time-step dependent local energy and quantum drift cutoffs,[34] and the Assaraf et al.[35] population control procedure. A weighted linear regression was used to extrapolate to zero time step to eliminate the time-step bias which, given the nature of the Umrigar et al. algorithm[15] should be very small at these time steps. The LDA single determinants were constructed using Kohn−Sham orbitals obtained from LDA/TZP calculations using the ADF DFT program.[29–31] A polarized valence triple-ζ (TZP) Slater-type basis set[28] was chosen for compactness, which is an increasingly important consideration with molecule size.

The HF single determinant trial wave functions were constructed from canonical HF orbitals, restricted HF (RHF) for C_2H_2 and restricted open-shell HF (ROHF) for C_2H, obtained from the GAMESS ab initio package.[36] Since GAMESS is restricted to Gaussian basis sets, a Slater TZP basis set[28] was fit to a large Gaussian basis set expansion; see Supporting Information Tables 1 and 2. The latter basis set was used in GAMESS to generate the MOs. The quality of the fit was checked by comparing variational Monte Carlo calculations using both the Slater basis and the Gaussian fit basis. These calculations agreed to within 1 millihartree of each other and with the GAMESS energy. For the DMC calculations, the Slater basis set was used. Based on past experience, the difference arising from the use of the Slater TZP basis set in place of the Gaussian basis is negligible.

The BOVB ab initio wave functions were constructed using the XMVB package,[37,38] and formed the determinantal part of the DMC trial wave function. For the ethynyl (C_2H) radical, strong spin contamination at the UHF level was detected. Orbital analysis showed that the spin contamination arises from strong spin symmetry breaking of the UHF π orbitals, indicating a lack of correlation in the π system at the single-determinant level. We suspected that this could be a significant source of nodal error. Therefore we decided to treat the two π bonds as the active space in the VB calculations. Each π bond was expressed in terms of covalent and ionic VB structures. The σ system (both the C−C and the C−H bonds, and the orbital containing the radical electron) were described by delocalized MOs. The carbon core orbitals were frozen, and taken from a ROHF calculation. This description leads to a 9-VB-structure expansion, however, two $C^{2+}C^{2-}$ double ionic structures were discarded, resulting in a 7-VB-structure wave function (14 determinants).

We used different sets of orbitals for different VB structures enabling each active atomic orbital to undergo polarization, rehybridization and size changes, which introduces static and some dynamic electron correlation. For acetylene, a similar BOVB description to that for the ethynyl radical was followed. The two π bonds were included in the active space along with one of the C−H σ bonds, and expressed in terms of covalent and ionic VB structures. The remaining C−H and C−C σ bonds were left in terms of delocalized MOs (from a RHF calculation) and not included in the VB active space. This treatment gives a total 21 VB structures (56 determinants) that were used to construct the DMC trial wave function. Each group of seven structures corresponding to a specific situation for the active C−H bond (ionic or covalent) share the same set of orbitals, and different set of orbitals are used for different groups of VB structures. Based on this construction of our BOVB wave function, we shall refer to these wave functions as partial-breathing-orbital valence bond (p-BOVB). This is to distinguish with the higher level SD-BOVB defined by Hiberty et al.,[20] where all orbitals are different for each VB structure, and the orbital pair describing the C−H bond is split into two singlet-coupled orbitals for each ionic group of VB structures. Explicit forms of the p-BOVB and SD-BOVB wave functions suitable for DMC calculations are given in the Supporting Information.

2.2. Geometries. Molecular geometries were obtained at the B3LYP/cc-pVTZ level of theory using the Gaussian 03 software package.[39] This procedure was followed to be consistent with the previous DMC hydrocarbon BDE study.[23] Owing to the linearity of both C_2H and the C_2H_2, only the carbon−carbon (R_{CC}) and carbon−hydrogen (R_{CH}) bond distances need to be specified.

For ethynyl radical, the C−C bond distance in the DMC calculations was set to 1.199 Å and the C−H bond distance was fixed at 1.060 Å. These are to be compared with the NIST[40] recommended experimental values of 1.217 Å for the C−C bond distance and 1.047 Å for the C−H bond distance. Barnett et al. reported 1-CSF DMC energies at two geometries for this system. At the DMC level using only an 1-CSF trial function, the first geometry (R_{CC} = 1.216 Å and R_{CH} =1.071 Å) was 1.5 ± 0.5 kcal/mol higher in total energy than the second geometry (R_{CC} = 1.221 Å and RCH = 1.067 Å).[19] The latter geometry was used by Barnett et al. for their multi-CSF DMC calculations.

For acetylene, B3LYP/cc-pVTZ gave a R_{CC} of 1.196 Å and a R_{CH} of 1.062 Å. This geometry is closer to the NIST[40] recommended experimental geometry (R_{CC} = 1.203 Å and R_{CH} = 1.063 Å) than the geometry used in the Barnett et al. study (R_{CC} = 1.180 Å and R_{CH} = 1.054 Å).

Frozen core restricted shell coupled cluster with singles doubles and perturbative triples excitations,[41] with the Dunning correlation-consistent polarized valence quadruple-ζ basis set[42] (RCCSD(T)/cc-pVQZ), single point energy calculations were performed for each of the aforementioned geometries using Q-Chem 3.0[43] to estimate the effect of geometry on the DMC energy. Of the two geometries for C_2H reported by Barnett et al., the first geometry (R_{CC} = 1.216 Å and R_{CH} =1.071 Å) was 0.8 kcal/mol higher in energy at the RCCSD(T)/cc-pVQZ level of theory than the second geometry and 2.7 kcal/mol lower than the B3LYP/cc-pVTZ geometry. The energy at the NIST[40] recommended experimental geometry was 2.6 kcal/mol lower than that at the B3LYP/cc-pVTZ geometry. For C_2H_2, a RCCSD(T)/cc-pVQZ calculation gives an energy at the experimental geometry that is 0.1 kcal/mol lower than that at the B3LYP geometry, and 0.9 kcal/mol lower than that at the geometry used by Barnett et al. Based on CCSD(T) calculations for C_2H and C_2H_2, we estimate the difference in geometries between Barnett et al. and the present study could produce an energy descrepancy of as much as 4 kcal/mol in the C−H BDE.

2.3. Thermochemistry. Atomization energies are challenging to compute accurately, since one needs to recover ideally equal percentages of the electronic correlation energy for both the atoms that comprise the molecule and the molecule itself. Here we are concerned with the C−H bond dissociation energy [DH° (C−H)]. We calculate it directly from the DMC total energies at 0 K of C_2H [$E(C_2H)$] and C_2H_2 [$E(C_2H_2)$] from the following expression,

$$\mathrm{DH}^{\circ}(\mathrm{C-H}) = \Delta E + \Delta E_{\mathrm{ZPE}} + \Delta H_0^{298}(\mathrm{C_2H}) - \Delta H_0^{298}(\mathrm{C_2H_2}) + \Delta_f H^{\circ}_{298}(\mathrm{H}) - \Delta_f \mathrm{H}^{\circ}_0(\mathrm{H}) \quad (1)$$

where ΔE is defined by

$$\Delta E = E(\mathrm{H}) + E(\mathrm{C_2H}) - E(\mathrm{C_2H_2}) \quad (2)$$

and ΔE_{ZPE} is the difference in zero-point vibrational energies (E_{ZPE}) of the C_2H and C_2H_2 molecules:

$$\Delta \mathrm{ZPE} = E_{\mathrm{ZPE}}(\mathrm{C_2H}) - E_{\mathrm{ZPE}}(\mathrm{C_2H_2}) \quad (3)$$

The B3LYP/cc-pVTZ harmonic frequencies were obtained using Gaussian 03 to yield ZPEs and thermal corrections (ΔH_0^{298}) from 0 to 298 K. The ZPEs where scaled by 0.9897.[23] The experimental enthalpies of formation for the hydrogen atom at 0 K, $\Delta_f H_0(\mathrm{H})$ = 51.634 ± 0.001 kcal/mol, and 298 K, $\Delta_f H_{298}(\mathrm{H})$ = 52.103 ± 0.003 kcal/mol, were obtained from ref 44 and refs 45, 46, respectively. The thermal corrections for species X are defined by

$$\Delta H_0^{298}(\mathrm{X}) = \Delta_f H^{\circ}_{298}(\mathrm{X}) - \Delta_f \mathrm{H}^{\circ}(\mathrm{X}) \quad (4)$$

and in our calculations correspond to $\Delta H_0^{298}(\mathrm{C_2H})$ of 0.77 kcal/mol and $\Delta H_0^{298}(\mathrm{C_2H_2})$ of 0.01 kcal/mol. These corrections in addition to the scaled B3LYP/cc-pVTZ ZPEs of 10.37 kcal/mol for C_2H and 16.76 kcal/mol for C_2H_2 result in a −5.2 kcal/mol thermal-vibrational correction factor to the dissociation reaction energy, ΔE, to obtain the C−H BDE, DH° (C−H). The choice of ZPEs is expected to change the computed BDE by less than 2 kcal/mol.

3. Results and Discussion

In Table 1 ab initio basis-set calculated total energies for acetylene and ethynyl radical are given along with the corresponding C−H BDEs. In Table 2 we give corresponding values from DMC calculations. These values are compared with the recommended experimental C−H BDE[47] and exact total energies as estimated by Barnett et al.[19] All computations in these tables were performed at the B3LYP/cc-pVTZ geometry and BDEs where computed using the methodology described in Section 2.3. The poor HF result is expected, given the absence of electron correlation, and gives a C−H BDE in error from the recommended experimental value of 132.8 ± 0.7 kcal/mol by 20.7 kcal/mol. The second column of Table 1 shows that the p-BOVB wave function recovers a moderate percentage of the total correlation energy (19.2% for C_2H and 19.9% for C_2H_2). The C−H BDE is in error with respect to the experiment by 14.8 kcal/mol. Better agreement with experiment is obtained using a more sophisticated BOVB wave function, as shown in the third column. The SD-BOVB method predicts a BDE of 127.2 kcal/mol, which deviates from the experimental value by 5.6 kcal/mol. However, as mentioned earlier we sought VB wave functions that are compact and simple for use as DMC trial wave functions. For this reason the simpler p-BOVB wave functions were used in the DMC calculations. For comparison, we have included CCSD(T) with the TZP and the quadruple-ζ cc-pVQZ basis sets in Table 1. With the TZP basis set, CCSD(T) recovers a substantially larger amount of correlation energy than BOVB (60.3% and 61.4% for ethynyl radical and acetylene, respectively). However, the CCSD(T)/TZP predicted BDE differs by 4.6 kcal/mol from the experimental value, which is only slightly better than that at the SD-BOVB level. Using the larger cc-pVQZ basis set, CCSD(T) predicts a BDE lying within 1.3 kcal/mol of experiment.

Table 2 presents DMC BDEs obtained using various trial functions. The first column gives our (DD and WAL) previously reported[23] findings with a HF trial function. In that study, the Partridge #2 basis-set[48] was used along with soft ECPs[49] so that the resultant energies are valence energies as opposed to all-electron total energies. For this reason, the column entries are left blank. The acetylene C−H BDE obtained in that study was 136.6 ± 0.1 kcal/mol which is consistent with our zero-time-step extrapolated value of 137.5 ± 0.5 kcal/mol (second column). It is important to note that the DMC results from the Kollias et al. study are for a single small time step and are not extrapolated to zero time step. If we use energies from only a single time step to compute the C−H BDE, we obtain BDEs in the range of 136.3−137.5 ± 0.4 kcal/mol for DMC with the HF/TZP trial wave functions (second column).

In the third column the single-determinant wave functions are constructed from LDA/TZP Kohn−Sham orbitals. The DMC computations that used these orbitals recovered the most correlation energy for both acetylene and ethynyl radical. The DMC BDE improved to 135.6 ± 0.5 kcal/mol. The benefits of using DFT orbitals for DMC computations has been examined in several previous studies; for example, refs 50, 51.

Examination of time step extrapolations in Figures 1 and 2 shows that the greatest effect occurs for C_2H_2 with LDA/TZP orbitals in a single determinant trial function. If only single time-step energies were used to compute the BDE, then results would lie in the range of 133.6−134.9 ± 0.5 kcal/mol, and be in slightly better agreement than the zero time step extrapolated value. Note that all of the single determinant DMC calculations systematically overestimate the BDE, which implies that a larger amount of the correlation energy is recovered by DMC for acetylene than for ethynyl radical. The difference in percentage of the correlation energy recovered for ethynyl radical compared to acetylene, is 1.9 ± 0.2% for DMC with HF orbitals and 1.2 ± 0.2% for DMC with LDA orbitals.

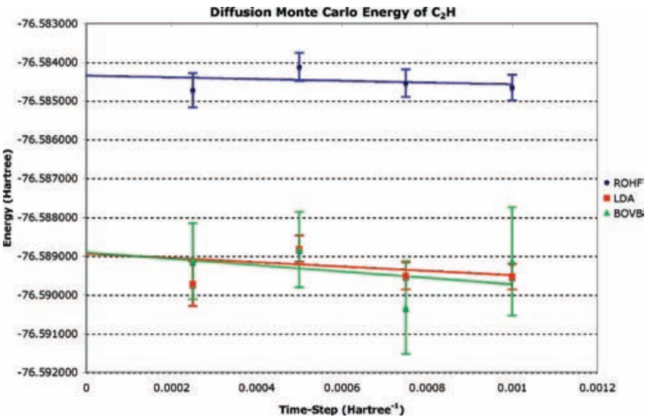

Figure 1. DMC total energies for C_2H using ROHF, LDA, and BOVB trial wave functions. Extrapolation to zero time step performed using a weighted linear regression fit.

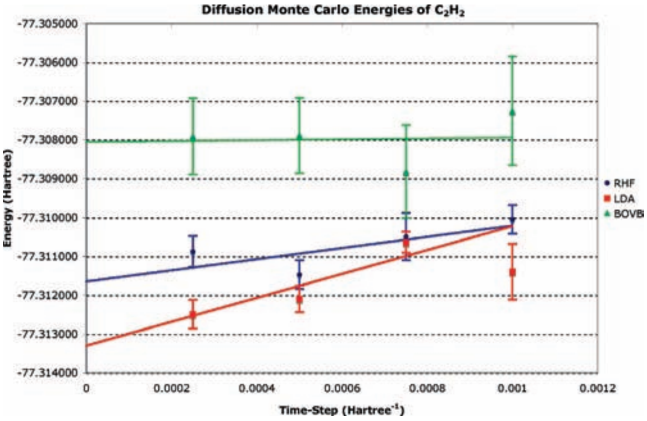

Figure 2. DMC total energies for C_2H_2 using RHF, LDA, and BOVB trial wave functions. Extrapolation to zero time step performed using a weighted linear regression fit.

DMC with the p-BOVB trial wave functions recovered 1.0 ± 0.3% more of the correlation energy for ethynyl radical than DMC with a HF trial wave function. The BDE obtained from the p-BOVB DMC energies is in excellent agreement with experiment. As seen in Figures 1 and 2 the effect of extrapolating to zero time step is not a significant factor in the DMC BDE for this trial wave function. In addition to the increase in percentage correlation energy recovered for the ethynyl radical, DMC with p-BOVB as a guiding function recovered 0.8% ± 0.4% less correlation energy for acetylene than DMC with HF. The p-BOVB DMC recovered essentially the same percentage of correlation energy for both acetylene and ethynyl radical. This near perfect balance in correlation energy recovered for both species explains the excellent agreement with the experimental BDE.

In contrast to the truncated MCSCF-based trial wave functions of the Barnett et al. DMC study,[19] the p-BOVB wave function is more compact and introduces a modest amount of correlation to correct for the multireference character of the π bonds and to describe the C−H dissociation. It is able to describe both acetylene and ethynyl radical consistently.

The use of VB methods also avoids arbitrary truncation of multideterminant trial wave functions. Truncation of MCSCF wave functions based on CSF coefficient values can produce an unbalanced description of the rectants and products in a bond dissociation reaction leading to small improvement or even deterioration in DMC energies.[52,53] BOVB methods can be used to construct trial wave functions that remove spin contamination, and incorporate the necessary nondynamical correlation needed to properly describe the bond breaking or bond formation.

4. Conclusions

In this present DMC study we have found substantial improvement in the carbon−hydrogen bond dissociation energy (BDE) of acetylene using multideterminantal p-BOVB trial wave functions compared to single-determinantal trial wave functions obtained from HF and LDA. The p-BOVB-based DMC calculations result in a C−H BDE that is in excellent agreement with the recommended experimental value. Further DMC studies are necessary to determine if other VB trial wave functions offer systematic improvement over single-determinantal trial wave functions for acetylene as well as other hydrocarbons.

5. Acknowledgments

The authors thank Dr. Alexander C. Kollias for providing his basis-set fitting program that was used for fitting the TZP Slater basis to the large Gaussian basis expansion. Professor Wei Wu is most gratefully acknowledged for providing the XMVB code. WAL was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences, Geosciences and Biosciences Division of the U.S. Department of Energy, under Contract No. DE-AC03-76F00098. D.D. was supported by the CREST Program of the National Science Foundation under Grant No. HRD-0318519. The calculations were carried out at the National Energy Research Supercomputer Center (NERSC), which is supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

Supporting Information Available: Tables 1−2 contain the Gaussian basis sets that were used in the ab initio basis set calculations for carbon and hydrogen. Tables 3 and 4 contain the determinant coefficients for the p-BOVB wave functions of C_2H and C_2H_2. Tables 5 and 6 contain the molecular orbitals for the p-BOVB wave functions. Tables 7−10, contain the same information for the SD-BOVB wave functions. This material is available free of charge via the Internet at http://pubs.acs.org.

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JP8020062