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Diffusion Monte Carlo Study of Bond Dissociation Energies for BH_2, $B(OH)_2$, BCl_2, and BCl

Hui-ran Li[a], Xin-lu Cheng[a], Hong Zhang[a,b*]

a. Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065, China
b. College of Physical Science and Technology, Sichuan University, Chengdu 610065, China

On basis of bond dissociation energies (BDEs) for BH_2, $B(OH)_2$, BCl_2, and BCl, the diffusion Monte Carlo (DMC) method is applied to explore the BDEs of HB−H, HOB−OH, ClB−Cl, and B−Cl. The effect of the choice of orbitals, as well as the backflow transformation, is studied. The Slater-Jastrow DMC algorithm gives BDEs of 359.1±0.12 kJ/mol for HB−H, 410.5±0.50 kJ/mol for HOB−OH, 357.8±1.46 kJ/mol for ClB−Cl, and 504.5±0.96 kJ/mol for B−Cl using B3PW91 orbitals and similar BDEs when B3LYP orbitals are used. DMC with backflow corrections (BF-DMC) gives a HB−H BDE of 369.9±0.12 kJ/mol which is close to one of the available experimental value (375.8 kJ/mol). In the case of HOB−OH BDE, the BF-DMC calculation is 446.0±1.84 kJ/mol that is closer to the experimental BDE. The BF-DMC BDE for ClB−Cl is 343.2±2.34 kJ/mol and the BF-DMC B−Cl BDE is 523.3±0.33 kJ/mol, which are close to the experimental BDEs, 341.9 and 530.0 kJ/mol, respectively.

Key words: Bond dissociation energy, Diffusion Monte Carlo method, Choice of orbitals, Backflow transformation

I. INTRODUCTION

The boron-hydrogen complexes become especially interesting because of their applications in hydrogen storage. Boron hydrides transform to ionic or covalent compounds, such as the ammonium borohydride salt $BH_4^-NH_4^{+2}$ [1] and ammonia borane NH_xBH_x (x=1−4), as hydrogen storage materials [2]. Hydroxyborons, such as $B_3O_3H_3$ [3] and $B(OH)_2$, can be produced in the reaction of $H_2O(g)$ with elemental boron when there are suitable conditions. They play an important role in regeneration cycles of hydrogen storage materials [4]. And boron halides, such as BF_3 and BCl_3, play a vital role in the development of plasma-assisted fabrication of microcircuits, semiconductor and telecommunication industries [5].

Over the past years, the boron-containing molecular systems have been studied extensively both experimentally and theoretically [6]. For example, Komatsu and Moriyoshi have investigated the transition from thermal- to electron-impact decomposition of diborane experimentally [7]. Recently, Grant and Dixon predicted the bond dissociation energies (BDEs) of some borane compounds using the frozen core CCSD(T) method [8]. Judging from the previous works, we notice that some calculations are in agreement with the values

derived from the experiments [8, 9]. But large discrepancies between experimental and theoretical values still exist [8]. There are more than one available experimental BDEs for HB−H (459.4 kJ/mol [6], 375.8 kJ/mol [10]), ClB−Cl and B−Cl also have several different experimental results. However, the theoretical HB−H BDE given by Grant and Dixon is 331.5 kJ/mol, using CCSD(T)/aVQZ method. For HOB−OH, the recommended experimental BDE is 507.0±29.3 kJ/mol [6], but the prediction of Grant and Dixon is 398.8 kJ/mol.

It is well known that some species can not be easily handled [11, 12], and it can be difficult to determine the BDEs experimentally. The values obtained by different methods may be different from each other, and the discrepancies may be great for some molecules. For example, there are two strikingly different experimental HB−H BDEs, *i.e.* 459.4 and 375.8 kJ/mol. On the level of theory, the accuracy of each form is not universal. For instance, the density functional theory applies the space distribution of the electron to solve the Schrödinger equation [13], and introduces exchange correlation functions to include the effects of electron correlation. But the choice of correlation functional and parameters can strongly affect the results of BDEs in DFT calculations, for the correlation effects occupy an important part of the energy content [14]. Therefore, the theoretical approximation may provide qualitatively wrong BDEs sometimes. Yao *et al.* found that only MPW1P86 and (RO)B3P86 can offer better results, when they applied five DFT methods to compute

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*Author to whom correspondence should be addressed. E-mail: hongzhang@scu.edu.cn, Tel.: +86-28-85418565

the BDEs for C−H, C−C, and so on [15]. Luo *et al.* pointed out that the DFT method always underestimates the energy of chemical bond [13]. Meanwhile, in the reactions concerning radical intermediates, there is no quantity more important than the hemolytic BDE [16]. The reliable BDEs are important for the thermodynamic analysis of reaction chemistry. By comparing with the accurate theoretical value, we can also decide which one is the most reliable among the available experimental values. It is necessary to apply high-level theoretical calculations to obtain the accurate BDEs for HB−H, HOB−OH, ClB−Cl, and B−Cl.

Quantum Monte Carlo (QMC) method is one of the high-level theoretical calculation methods [17, 18], which qualitatively describe the electronic structures. There are two typical calculations, the variational Monte Carlo (VMC) method and the diffusion Monte Carlo (DMC) method, included in the QMC approaches. The VMC method is based on the theory of variation method. The choice of the trial wave function can strongly affect the quality of VMC calculations, and there is a difficulty in choosing the accurate trial wave function. But DMC is more advanced, it projects out the ground state from a trail wave function [19]. In DMC method, the trial node is fixed (*i.e.* the so-called fixed-node approximation) to ensure the sampled distributions are non-negative. The fixed-node DMC solves the many-electron stationary state Schrödinger equation with imaginary time evolution. Therefore, the DMC calculation does not so strongly depend on the accuracy of trial wave function, which is just different from VMC. The DMC method can exactly estimate the ground state energies of many systems. For example, Wang *et al.* accurately computed the phenol O−H BDE using the DMC method, and they found that for single determinant trial wave function, the choice of orbitals can not strongly change DMC computed results [20].

In this work, Gaussian 03 [21] and CASINO ver 2.8.0 [22] packages are used to study the BDEs of HB−H, HOB−OH, ClB−Cl, and B−Cl. We attempt to obtain more accurate BDEs using DMC.

II. COMPUTATIONAL DETAILS

A. Geometries and thermochemistry

The geometry of each species is completely optimized using B3LYP/6-311(d,p). Figure 1 shows the calculated geometries. RB3LYP and UB3LYP are used for the close-shell and open-shell species, respectively. In the case of the open-shell species, each value of S^2 is 0.75, which indicates that there is no spin contamination in the pure doublet states. When the geometry structures are being optimized, the corresponding frequencies are also computed at the same level. When making an analysis of the frequency calculations, it can be noticed that there are no imaginary frequencies, which implies that
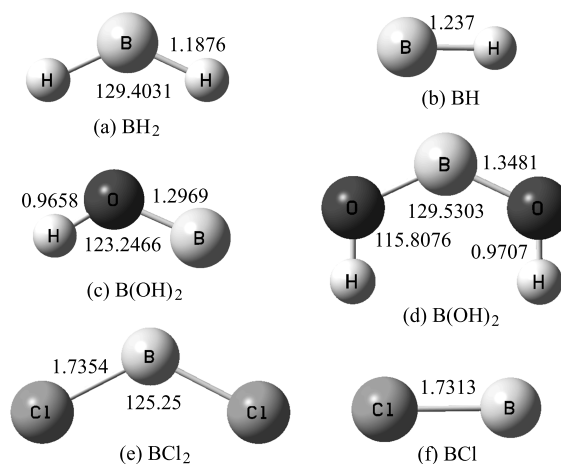

FIG. 1 The optimized geometries of the relevant boron-containing species at B3LYP/6-311(d,p) level of theory. Distances are given in Å, angles in (°).

the structure of each species is equivalent to a local minimum on the potential energy surface.

The BDE is defined as the change of enthalpy in the dissociation reaction. During the dissociation reaction, the chemical bond homolytically breaks and the dissociation fragments depart the parent molecules. The reaction can be described as follows:

$$AB \rightarrow A\cdot + B\cdot \quad (1)$$

At 298.15 K the BDE is the change of formation heats of the dissociated species, just as,

$$E_{\text{BDE}}^{298.15} = \Delta_f H_{298.15}(A\cdot) + \Delta_f H_{298.15}(B\cdot) - \Delta_f H_{298.15}(AB) \quad (2)$$

And the BDE at 0 K is defined as the difference of the zero-point-corrected energy between the parent molecule and the radicals and computed from,

$$E_{\text{BDE}}^{\ominus} = \Delta E + \Delta E_{\text{ZPE}} \quad (3)$$

where ΔE is defined by:

$$\Delta E = E(A\cdot) + E(B\cdot) - E(AB) \quad (4)$$

ΔE_{ZPE} is the difference in zero-point vibrational energies E_{ZPE} of the reactant and products at B3LYP/6-311(d,p) level, namely,

$$\Delta E_{\text{ZPE}} = E_{\text{ZPE}}(AB) - E_{\text{ZPE}}(A\cdot) - E_{\text{ZPE}}(B\cdot) \quad (5)$$

E_{ZPE} is obtained during the B3LYP/6-311(d,p) frequency calculations. The electronic energies of the relevant species are calculated using the high-level theoretical calculation approach, DMC method, at the B3LYP/6-311(d,p) geometries. For comparison, B3LYP, CBS-Q, G3, and CBS-QB3 implemented Gaussian 03 software are also used to compute the single point energies. The electronic energy of hydrogen atom which is needed in the calculation of HB−H BDE is fixed as 0.5 Hartree [23−25].

TABLE I Calculated BDEs (in kJ/mol) at different levels of theory.

	B3LYP	CBS-Q	G3	CBS-QB3	CCSD(T) [7]	Experimental values
HB−H	360.7	325.2	329.8	324.8	331.5	459.4 [5], 375.8 [9]
HOB−OH	407.1	378.3	377.0	380.0	398.8	507.0±29.3 [5]
ClB−Cl	326.9	331.1	323.1	330.3	327.7	341.9 [5], 388.7 [36]
B−Cl	484.9	512.1	507.9	511.2	505.8	510.8±4.6 [37], 530.0 [38], 539.2 [5]

B. Trial wave function construction and DMC

Gaussian 03 is used to generate the B3PW91 and B3LYP orbitals. Restricted shell wave functions are used for the close-shell molecules, and we use the unrestricted open shell wave functions for the open-shell species. As for the open-shell species, there is no high spin state in the ground state wave functions, because our unrestricted calculations have no spin contamination. This indicates that the trail wave functions of the open-shell species are reasonable. In this study, we provide different structures of the nodal surface of the wave function. The Gaussian wave functions, B3PW91 and B3LYP are used to construct the trail wave functions, respectively. And each of our trail wave functions is in the form of single determinant.

During the optimization of the trial wave function, the parameters are optimized at VMC level. The parameters (isotropic electron-electron terms μ, isotropic electron-nucleus terms χ and isotropic electron-electron-nucleus terms f), which are included in the Jastrow factor [26], are optimized using variance minimization. The cutoff length is also optimized in the process of variance minimization, since it can greatly affect the value of energy and that of variance [27]. Because of the fixed-node error in the DMC algorithm, the energies obtained by DMC are always higher than the ground-state energies if the fixed nodal surface is not exact. When the fixed-node errors of the initial compounds and radicals are not comparable, we have a difficulty in obtaining the accurate BDEs. For this reason, if the fixed-node error can be effectively reduced, some further improvements may be generated.

The backflow transformation can modify the nodal surface of the trial wave function and reduce the fixed-node error [28−32]. By introducing the backflow corrections, the trial wave function can have further correlations, the coordinate of the particle i contains both the position of electron and the backflow displacement of it [27]. In the ground state energy, the correlation energy which is missed by the Slater-Jastrow DMC (SJ-DMC) algorithm can be recovered with this method. According to this, the backflow transformation is introduced to B3LYP orbitals to make a further investigation. The parameters in the backflow are optimized by the filtered reweighted variance minimization [33]. Therefore, the wave function, which is constructed by B3LYP orbitals, is changed from the SJ form to BF form, and the SJ-

TABLE II Calculated BDEs (in kJ/mol) at DMC level.

	SJ-DMC[a]		BF-DMC[b]
	B3PW91	B3LYP	B3LYP
HB−H	359.1±0.12	356.1±1.00	369.6±0.12
HOB−OH	410.5±0.50	402.5±0.67	446.0±1.84
ClB−Cl	357.8±1.46	354.0±2.09	343.2±2.34
B−Cl	504.5±0.96	511.2±0.75	523.3±0.33

[a] The calculations are done without the backflow transformation.
[b] The calculations are performed with the backflow transformation.

DMC calculation is changed into DMC with backflow corrections (BF-DMC). It is expected that the remaining errors could be gradually eliminated.

An all-election calculation is performed in DMC (*i.e.* no pseudo potential is introduced in our computations) to make our calculations more accurate. Our DMC calculations are carried out at the effective time step of 2×10^{-4} Hartree^{-1}. With the purpose of maintaining a high acceptance ratio in DMC algorithm, we use the algorithm of Reynolds *et al.*, in the configuration space, only one electron is moved at a time [34], replaced of moving all electrons. In our DMC method, the move-acceptance ratio is around 99.9%. After the move of each electron, the configuration will be checked whether it has been out of the node surface, it will be rejected if it is out of the node surface [35].

III. RESULTS AND DISCUSSION

The HB−H, HOB−OH, ClB−Cl, and B−Cl BDEs computed by different theoretical methods are presented in Tables I and II. All of the calculations are corrected by the zero-point vibrational energies, on the purpose of improving the computed BDEs.

From Table I, we can see that the HB−H BDE computed by B3LYP method is 360.7 kJ/mol, which is closer to the experimental value of 375.8 kJ/mol. But it must be noted that there is more than one experimental BDE for HB−H. What's more, it is well known that the exchange correlation functional of B3LYP is not universal. Considering the limitation of B3LYP method, we can not make sure which experimental value is more reliable at B3LYP level, though the B3LYP calculation is

close to the experimental value of 375.8 kJ/mol.

As regards HOB−OH, our B3LYP calculation is 407.1 kJ/mol, which is better than other methods. But the discrepancy between the experimental value and theoretical value is still great. We consider the reason is that the recovering correlation energies in the reactants and products are not comparable, and the unbalance in the recovering correlation energies affects the HOB−OH BDE.

Table I indicates that the theoretical BDEs for ClB−Cl are similar to each other and all of the values are around 341.9 kJ/mol. However, the BDE for B−Cl obtained by B3LYP method is far different from the results obtained by the other four methods.

In Table I, we can also see that the BDEs computed by CBS-Q, G3, and CBS-QB3 methods are generally in agreement with one another, for HB−H, HOB−OH, ClB−Cl, and B−Cl, respectively. The three methods can not make an improvement in the BDEs for the studied compounds compared to the CCSD(T) method used by Grant and Dixon [8]. And the BDEs obtained by the composite *ab initio* methods are poor and all of the calculated results differ dramatically from the experimental BDEs for HB−H and HOB−OH. Therefore, in this study, DMC is applied to make a further investigation.

In Table II, we have compiled the BDEs calculated by SJ-DMC and BF-DMC. It must be noticed that our B3PW91 SJ-DMC BDEs are in reasonable agreement with the B3LYP SJ-DMC BDEs. Our DMC calculations just testify the conclusion of Wang *et al.*: for single determinant trial wave functions, using different orbitals obtained by different methods can not substantially affect DMC calculations [20].

All of the DMC calculations for HB−H BDE are close to the value of 375.8 kJ/mol obtained by experiment. The theoretical BDEs calculated by SJ-DMC using different trail wave functions agreed well with each other. The BF-DMC improves HB−H BDE to 369.6±0.12 kJ/mol that is closer to 375.8 kJ/mol. The HB−H BDE obtained from BF-DMC method is 47.7±0.12 kJ/mol higher than that given by HF method. It indicates that BF-DMC using B3LYP orbitals can recover the exchange correlation energy as much as 47.7±0.12 kJ/mol in HB−H BDE. Judging from our SJ-DMC and BF-DMC HB−H BDEs, the experimental value, 375.8 kJ/mol, is more reliable and should be recommended.

For HOB−OH, the SJ-DMC results obtained using B3PW91 orbitals and B3LYP orbitals are 410.5±0.50 and 402.5±0.67 kJ/mol, respectively. But the SJ-DMC HOB−OH BDEs are still not satisfying, even though a large amount of correlation energy has been recovered by SJ-DMC. It shows that the SJ-DMC has some difficulties to predict the exact ground state energy sometimes, and the difference is uniquely due to the so-called fixed-node approximation. We believe the problem is that the fixed-node error of the reactant and products is not small enough. It is necessary to introduce the

backflow correlations to the orbital part. As soon as the backflow parameters are introduced to the trail wave functions, *i.e.* SJ-DMC is changed to BF-DMC, we indeed have an excellent improvement in HOB−OH BDE, which can be seen in Table II. Using the same method as above-mentioned in HB−H, for HOB−OH BDE, the exchange correlation energy recovered by B3LYP BF-DMC is 147.6±1.84 kJ/mol. Compared to the B3LYP SJ-DMC calculated result, there is a recovered energy of 43.5±1.84 kJ/mol in HOB−OH BDE. The BF-DMC method gives the best calculation for HOB−OH among the approaches applied. It implies that the backflow transformation can effectively reduce the fixed-node error and give more reliable prediction.

It can be seen that the choice of orbitals can not substantially affect the SJ-DMC BDEs of ClB−Cl and B−Cl, just like the results of HB−H and HOB−OH. According to the BF-DMC ClB−Cl and B−Cl calculations, it can be said that the experimental BDEs of ClB−Cl (341.9 kJ/mol) and B−Cl (530.0 kJ/mol) are reliable.

IV. CONCLUSION

In the present work, the B3PW91 SJ-DMC BDEs are in reasonable agreement with the B3LYP SJ-DMC BDEs, and it implies that different orbitals which are used to construct the single determinant trail wave functions can not strongly change DMC results. For the BDE of HB−H, our DMC BDEs are in the range from 356.1±1.00 kJ/mol to 369.6±0.12 kJ/mol. All of the DMC calculations are close to the experimental value of 375.8 kJ/mol. Judging from our calculations, the experimental HB−H BDE, 375.8 kJ/mol, is more reliable than the other experimental value. As for HOB−OH, our SJ-DMC computed results are 410.5±0.50 kJ/mol and 402.5±0.67 kJ/mol using B3PW91 and B3LYP orbitals, respectively, which shows that the choice of nodes can not make a further improvement in HOB−OH BDE. But BF-DMC gives a value of 446.0±1.84 kJ/mol that is far better than SJ-DMC calculations. It indicates that the backflow correlations can effectively reduce the fixed-node error, and the backflow transformation should be introduced to the orbital part to improve the prediction. Our BF-DMC BDE of ClB−Cl is 343.2±2.34 kJ/mol and that of B−Cl is 523.3±0.33 kJ/mol. And we consider that the experimental BDEs, 341.9 kJ/mol and 530.0 kJ/mol, might be reliable.

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