Bond Dissocation and Conformational Energetics of Tetrasulfur: A Quantum Monte Carlo Study[†]

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Variational Monte Carlo (VMC) and fixed-node diffusion Monte Carlo (DMC) calculations are performed for S_4. The effect of single- and multireference trial functions, as well as choice of orbitals, is investigated for its effect on the quality of the Monte Carlo estimates. Estimates of symmetric (two S_2 molecules) and asymmetric (S atom and S_3 molecule) bond dissociation are reported. The conformational change of S_4 from C_{2v} to D_{2h} defines a double-well potential and is also estimated. Multireference DMC with natural orbitals (DMC/NO) estimates the energy of the conformational change as 1.20(20) kcal/mol; the dissociation of the long S−S single bond is estimated at 21.1(1.3) kcal/mol, and the asymmetric bond energy is estimated as 53.2(2.4) kcal/mol. An estimate of the total atomization energy using multireference DMC/NO gives a value of 219.5(2.2) kcal/mol. The relative quality of result and implications for simplified trial function design are discussed.

1. Introduction

As noted in the introduction of our previous work,[1] tetrasulfur (S_4) is a species of interest in explorations of the chemistry of Earth's early atmosphere.[2−4] S_4 is proposed as a significant molecule in the formation of sulfur aerosols.[5] Significant experimental work has been applied to the spectroscopy of S_4,[6−10] and there have been significant theoretical studies of this species as well.[11−16] Much of this interest arises from attempts at resolving the question of identification of conformational minima, as there exists ab initio density functional work[17] that agrees with perturbation theory calculations that the global minimum is the rectangular D_{2h} form. This conclusion is in contradiction with a large body of work, both theoretical and experimental, that favors the C_{2v} structure.

Interest in applying quantum Monte Carlo (QMC) techniques to S_4 arises from some practial similarities to prior QMC work on the beryllium dimer.[18] Both species consist of only one element, and both S_4 and Be_2 have unique electronic structure features in the molecule and dissociation products. Some of the more significant differences between the two systems are S_4 is not a system amenable to all-electron QMC, S_4 dissociations and conformer energies do not have the very small energy difference estimated in the beryllium dimer study, and the geometric parameters of S_4 are not as easily determined. It is anticipated that this QMC study will provide additional insight to ideas in the development of simplified QMC trial functions. Specifically, we anticipate the study of S_4 conformers and dissociation products to provide opportunity to investigate the impact of orbital choice and number of determinants on the quality of the QMC results, with an emphasis on diffusion Monte Carlo (DMC). The issue of orbital choice and trial function development has been addressed with respect to the overall accuracy of the method.[19−23]

2. Methods

2.1. Variational Monte Carlo (VMC). There is a similarity between the Schrödinger equation in imaginary time ($\tau = \imath t$), written in atomic units,

$$\frac{\partial \Phi}{\partial \tau} = \frac{1}{2}\nabla^2 \Phi + V\Phi \tag{1}$$

and a classical diffusion equation with a rate term,

$$\frac{dC}{dt} = D\nabla^2 C + kC \tag{2}$$

In eq 1, Φ is a quantum mechanical wavefunction, and ∇^2 and V are the kinetic and potential energy operators respectively. In eq 2, C is the concentration, D is the diffusion constant, and k is a rate constant. When the quantum mechanical wavefunction in eq 1, serves as a probability density in imaginary time, no real time dynamics can be obtained.[24−28] Using Φ in this manner is analogous to considering it as a concentration of electrons undergoing rate and diffusion processes.

The conceptually simple variational Monte Carlo (VMC) method[29−32,34] uses Monte Carlo integration to evaluate a trial function. Unlike basis set expansion ab initio methods which rely on accurate integration of molecular integrals to achieve high accuracy, VMC trial functions may be of any form. In atomic and molecular applications, this trial function is often a product of a correlation function, which depends explicitly on interparticle distances, and a wave function usually computed in one of the following approximations: Hartree−Fock (HF), configuration interaction (CI), or complete active space self-consistent field (CASSCF). The probability distribution used in the Monte Carlo integration is taken as the square modulus

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of the trial function, and in all-electron VMC the energy is an upper bound to the exact energy of the state being evaluated. The form of the estimator used in VMC is:

$$\langle E\rangle = \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \frac{\left\langle\Psi\left|\frac{H\Psi}{\Psi}\right|\Psi\right\rangle}{\langle\Psi|\Psi\rangle} = \frac{\langle\Psi|E_L|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \langle E_L\rangle \quad (3)$$

where E_L is the "local energy", defined below. Of the various implementations of VMC referenced above, we choose to employ a drift and diffusion model using the Metropolis algorithm.

2.2. Diffusion Monte Carlo. The DMC method is based on stochastic simulation of the Schrödinger equation in imaginary time; the latter may be written:[35,27,28]

$$\frac{\partial f}{\partial t} = \frac{1}{2}\nabla(\nabla - F)f - (E_L - E_T)f \quad (4)$$

where the distribution

$$f \equiv \Psi_T\Phi \quad (5)$$

Here, Ψ_T is a known wavefunction, Φ is the exact solution, and

$$F \equiv \ln|\Psi_T|^2 \quad (6)$$

is labeled the quantum force. The parameter E_T is an energy offset, and

$$E_L(\vec{R}) \equiv \frac{\hat{H}\Psi_T(\vec{R})}{\Psi_T(\vec{R})} \quad (7)$$

is the local energy, where $\vec{R}$ denotes the 3N coordinates of the N electron system. We choose Ψ_T as the product of an independent-particle wavefunction, Ψ_0, and a correlation function U, that is,

$$\Psi_T = \Psi_0 \exp U \quad (8)$$

where

$$U \equiv U(r_{ij}, r_{i\alpha}) \quad (9)$$

In eq 9, the r_{ij} are electron−electron distances, and the $r_{i\alpha}$ are electron−nuclear distances. The parameter E_T is generally chosen to be close to the expected value of the local energy in order to reduce the magnitude of the last term on the right-hand side (rhs) of eq 4. The function F produces a drift in the simulation that increases sampling in the regions where the wavefunction is large. Since fermion statistics are not enforced, the wavefunction is prone to variational collapse. The fixed-node approximation prevents this by imposing the nodal structure of Ψ_T on Φ, thus ensuring that f is non-negative for all $\vec{R}$.

2.3. Trial Function Forms. In previous work,[18] the effect of trial function form on energy estimates was a significant theme. Lessons learned from that work are applied in the current study. Flexibility of choice in selection of the form of the QMC trial function requires a narrowed focus in trial function development. We chose to focus on varying the origins of the orbitals and determinants of the independent particle wavefunction, Ψ_0, and not the choice of Stevens, Basch, and Krauss (SBK)[33] effective core potentials (ECP) or correlation function. In the present study, the independent particle wavefunction, Ψ_0 was developed from a series of simple CI calculations. The correlation function is a Schmidt−Moskowitz[34] adaptation of the Boys−Handy function,[36] which includes terms describing two- and three-body interactions. The correlation function parameters were optimized by minimizing the value of the Manhattan functional.[37] The Manhattan functional minimizes the absolute value of the deviation from the trial energy instead of the variance. This approach does not square the contribution of outlying walkers to the optimized value, while retaining a lower limit of zero.[37] The researchers acknowledge that the optimal scheme for producing highly accurate trial functions includes optimization of the CI coefficients along with the parameters of the correlation function. In light of the goal of developing a simplified scheme for trial function design, we elected not to perform an optimization of CI coefficients and correlation parameters. For the species investigated, four trial functions were derived from two choices in trial function design: (1) the choice to use Hartree−Fock orbitals (HF) or CISD natural orbitals (NO's), and (2) the choice to use the Hartree−Fock single reference or a CISD multireference wavefunction.

3. Results

Initial geometry optimizations for the species S_4, S_3, and S_2 at the B3LYP/cc-pVTZ level were refined at the CCSD(T)/cc-pVQZ level. The geomertic parameters of S_4 are of particular interest for comparison against experimental determinations as well as other calculations. The geometric parameters from ref 1 were also used for this study. These parameters compared quite favorably to experiment and are included in Appendix 5. CISD calculations were performed using GAMESS and a modified cc-pVTZ basis. Orbitals from the restricted Hartree−Fock (HF) and CISD natural orbital (NO) calculations were used in construction of the trial wavefunction. VMC and DMC energies were calculated for relevant singlet and triplet states of S_3, S_2, and S atom. VMC and DMC energies, within the ECP approximation, were also calculated for the $^1A_1$ C_{2v} and ^1A_g D_{2h} conformers of S_4, to determine the depth of the double-well potential. ECP-DMC values reported here include an imaginary time step of $\tau = 0.001$, with time step bias tested using three time steps covering 2 orders of magnitude. Most of the multireference descriptions included only two determinants, given that the majority of species under investigation were well-behaved within their respective Hartree−Fock approximations. However, in some specific instances, the multireference description was important to the DMC calculation, as evidenced by a closer examination of the Hartree−Fock orbital energies. These cases are identified in section 4.

Figure 1 is an energy diagram (not to scale) of the states investigated in this study. All values shown in the figure are DMC results from using a natural orbital trial function with two determinants. The major focus of our efforts was the depth of the double-well potential, labeled as energy "A". This value compares favorably with the other computed values as presented in Table 1. In our investigation of S_4, the symmetric cleavage (energy "B", Table 2) and total cleavage (energy "E") are on the right side. The asymmetric cleavage of S_4 to a triplet excited-state of S_3 and atomic ground state sulfur (energy "C", Table 3) and subsequent energy of the ground state products (energy "D") are on the left side of the diagram.

The double-well potential is defined by the C_{2v} to D_{2h} transition. The performance of DMC here appears independent of the number of determinants in the trial wavefunction. The multireference QMC trial function in Table 1 used two determinants. It is important to note that the degradation of the

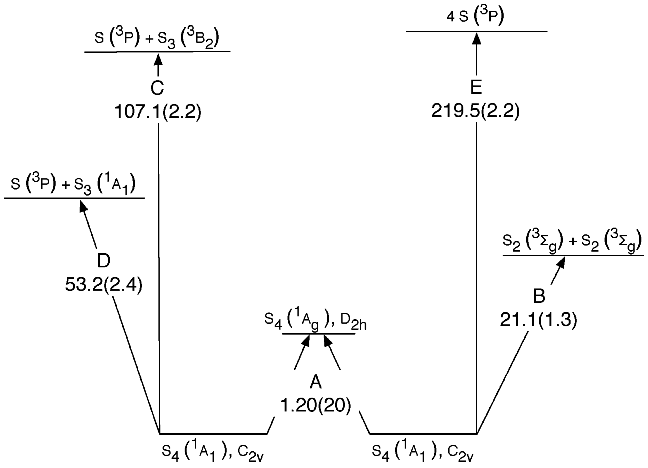

Figure 1. Energy level diagram for S_4 conformers and dissociation products (not to scale). Values in kilocalories per mole are multireference DMC with CISD natural orbitals.

TABLE 1: Values for Transiton A: C_{2v} to D_{2h}, in Kilocalories per Mole

method	transition energy, kcal/mol
VMC/HF orbitals, single-reference	3.12(6)
VMC/Natural orbitals, single-reference	1.51(7)
VMC/HF orbitals, multireference	5.0(8)
VMC/Natural orbitals, multireference	3.0(8)
G3X(MP2)[a] [38]	1.79
B3LYP/aug-cc-pVDZ//B3LYP/cc-pVDZ[b] [15]	2.11
B3LYP/cc-pVDZ//B3LYP/cc-pVDZ[b] [15]	1.26
CCSD(T)/aug-cc-pVDZ//B3LYP/cc-pVDZ[b] [15]	−0.16
CCSD(T)/cc-pVTZ[16]	1.52
CCSD(T)/cc-pVQZ[14]	1.85
CCSD(T)[1]	1.6
CASPT3(16,12)/6-31G*[a] [38]	1.15
MRCI-CASSCF(16,12)/6-31G*[a] [38]	1.27
DMC/HF orbitals, single-reference	2.89(25)
DMC/Natural orbitals, single-reference	1.35(25)
DMC/HF orbitals, multireference	1.87(20)
DMC/Natural orbitals, multireference	1.20(20)

[a] We also note that the study in ref 38 reports a series of CASSCF and CASPT values. The calculation in this series that recovers the most correlation energy for the C_{2v} structure is at the CASPT3(16,12)/6-31G* level, with a barrier of 1.15 kcal/mol, while the most highly correlated value comes from the MRCI-CASSCF(16,12)/6-31G* calculation. [b] These values are from the results in Table 2 of ref 15.

TABLE 2: Values for Transiton B: $S_4 \rightarrow S_2$ ($^3\Sigma_g$) + S_2 ($^3\Sigma_g$), in Kilocalories per Mole

method	bond energy, kcal/mol
VMC/HF orbitals, single-reference	15.5(1.6)
VMC/Natural orbitals, single-reference	26.5(1.4)
VMC/HF orbitals, multireference	45.1(5)
VMC/Natural orbitals, multireference	47.4(6)
B3LYP/aug-cc-pVDZ//B3LYP/cc-pVDZ[15]	9.66
CCSD(T)/aug-cc-pVDZ//B3LYP/cc-pVD[15]	13.4
G3X(MP2)[a] [38]	27.5
CCSD(T)[1]	22.8
DMC/HF orbitals, single-reference	36.1(3.6)
DMC/Natural orbitals, single-reference	29.1(3.0)
DMC/HF orbitals, multireference	22.0(1.6)
DMC/Natural orbitals, multireference	21.1(1.3)

[a] There were no corrseponding CASPT results reported for this energy in ref 38.

TABLE 3: Values for Transiton C: $S_4 \rightarrow S$ (^3P) + S_3 ($^3B_2$), in Kilocalories per Mole

method	bond energy, kcal/mol
VMC/HF orbitals, single-reference	116.1(8)
VMC/Natural orbitals, single-reference	113.0(9)
VMC/HF orbitals[a], multireference	104.9(9)
VMC/Natural orbitals[a], multireference	95.9(9)
DMC/HF orbitals, single-reference	151.6(2.1)
DMC/Natural orbitals, single-reference	129.5(2.5)
DMC/HF orbitals[a], multireference	105.8(2.4)
DMC/Natural orbitals[a], multireference	107.1(2.2)
estimated CCSD(T)[b] [1]	131.1, 130.4

[a] The absence of a complimentary S_3 ($^3B_2$) multireference description results in a severe underestimation of the reaction energy at both VMC and DMC levels. [b] CCSD(T) energy of transition D1 with experimentally determined S_3 excitation energies.[1,39,40,10]

TABLE 4: Values for Transiton D: $S_4 \rightarrow S$ (^3P) + S_3($^1A_1$), in Kilocalories per Mole

method	bond energy, kcal/mol
VMC/HF orbitals, single-reference	53.5(9)
VMC/Natural orbitals, single-reference	51.4(9)
VMC/HF orbitals[a], multireference	69.2(7)
VMC/Natural orbitals[a], multireference	76.3(6)
B3LYP/aug-cc-pVDZ//B3LYP/cc-pVDZ [(15)]	57.0
CCSD(T)/aug-cc-pVDZ//B3LYP/cc-pVDZ [(15)]	52.8
DMC/HF orbitals, single-reference	87.8(2.2)
DMC/Natural orbitals, single-reference	65.9(2.6)
DMC/HF orbitals[a], multireference	53.5(1.6)
DMC/Natural orbitals[a], multireference	53.2(2.4)
CCSD(T) [(1)]	64.0

[a] Variance in the determinants of the complimentary S_3 ($^1A_1$) multireference description also impacts the estimation of the reaction energy at both VMC and DMC levels.

quality of the VMC result is consistent with observations in a previous study of the beryllium dimer.[18] Both DMC/NO values are statistically indistinct and consistent with the slightly higher value of 1.6 kcal/mol reported by collaborators.[1] In addition, we note other comparable values have been reported by Sormova et al.,[14] Millefiori et al.,[15] and McCarthy et al.[16] that report slightly higher values for the transition. The G3X(MP2) values of Wong and Steudel[38] cited in the tables use QCISD-(T)/GTMP2 large instead of additivity at the MP2 level; for consistency with the original author, we elect to respect their notation. Of particular interest is the CCSD(T)/aug-cc-pVDZ//B3LYP/cc-pVDZ value that identifies the D_{2h} geometry as the minimum by less than two-tenths of one kilocalorie per mole.

DMC estimates of symmetric cleavage of S_4 are improved by use of a multireference description; with statistically indistinct DMC values for both types of orbitals. The multireference values are consistent with a slightly higher value of 22.8 kcal/mol reported by collaborators.[1] We anticipated that the single reference DMC estimates would vary from their multireference counterparts because of two factors: the differential recovery of correlation energy between S_4 and S_2; the decreases in the local energy estimates, after optimization, for multireference DMC were fairly insensitive to choice of orbitals. This behavior is observed for the other estimated energies.

The initial cleavage of the short S−S double bond leads to asymmetric products and increases the number of relevant species to three. Because these products are not all in their ground states, we also estimated the overall energy difference in Table 4. Again, we observe the sensitivity of the single-reference description to orbital choice resulting in two statistically distinct values at the DMC level. The need for consistent treatment of species is also evident in the multireference description; without corresponding trial functions for the molecule and atom, we observe a significant decrease in the quality of result for the multireference estimates.

TABLE 5: Values for Transiton E: $S_4 \rightarrow 4\ S(^3P)$, in Kilocalories per Mole

method	atomization energy, kcal/mol
VMC/HF orbitals, single-reference	174.5(7)
VMC/Natural orbitals, single-reference	175.6(8)
VMC/HF orbitals, multireference	186.5(7)
VMC/Natural orbitals, multireference	184.3(8)
B3LYP/aug-cc-pVDZ//B3LYP/cc-pVDZ[15]	204.08
CCSD(T)/aug-cc-pVDZ//B3LYP/cc-pVDZ[15]	181.09
DMC/HF orbitals, single-reference	133.3(2.0)
DMC/Natural orbitals, single-reference	133.8(2.5)
DMC/HF orbitals, multireference	224.2(2.3)
DMC/Natural orbitals, multireference	219.5(2.2)
CCSD(T)[1]	224.67, 226.80

The energy estimates of the dissociation products at their respective ground states in Table 4 provide further evidence of the effect of orbital choice and number of determinants. In this case, the CCSD(T) value of 64.0 kcal/mol reported in ref 1 more closely agree with the single reference DMC/NO result of 65.9(2.6) kcal/mol. We suspect that this may be due to differences in the number of determinants in the multireference descriptions for the three species.

The atomization energy, presented in Table 5, is largely insensitive to the choice of orbitals but significantly sensitive to an additional determinant in the trial wavefunction. For comparison, the multireference DMC values for total atomization energy of 224.2(2.3) and 219.5(2.2) kcal/mol are slightly below those reported in ref 1, while the single-reference descriptions significantly underestimate the energy. The following section discusses and analyzes the implications of the preceding results in the context of orbitals and determinants in QMC trial function design.

4. Discussion

This work can be approached in three parts: first, unique aspects of the electronic structure of S4 itself; second, the impact of orbital choice on the QMC energy estimates; and third, the more significant impact of number of determinants on the QMC energy estimates. Our intial observations of the bond dissociation energies was that the estimates were quite poor: with the exception of atomization energy, the single-reference Hartree−Fock results were not reasonably in range of other high-level theory. This observation ran counter to the presumption that S4 is completely described by a single RHF determinant. That assumption concealed a significant detail of RHF orbital energies; the lowest unoccupied molecular orbital (LUMO) is a bound state in the C_{2v} conformation. While this unique feature of the HF description did not cause problems for the double-well potential, it is significant in the dissociation energetics.

In the single reference descriptions, choice of orbitals is significant in the overall quality of result for absolute and relative energetics, particularly for DMC. The bound LUMO is not an artifact in that it remained bound with use of correlation consistent basis sets at the CCSD(T) level of theory. In order to properly describe the bond dissociation of tetrasulfur, multireference descriptions are necessary. By doing so, the importance of orbital choice between Hartree−Fock and natural orbitals is de-emphasized, an outcome that is consistent with the rationale for use of natural orbitals in single reference calculations. In most cases, occupancies derived from the CISD determinants proved better descriptors than a single reference with occupancies derived from Hartree−Fock methods.

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5. Appendix

The geometric parameters for S_4 are taken from ref 1. The QMC study uses extrapolated CCSD(T)/CBS(DTQ+d) values for the C_{2v} and D_{2h} structures. The sulfur−sulfur double bond length used for the rectangular structure (1.891 Angstroms) is from the CCSD(T)/aV5Z calculation.

molecule	basis/method	r(S=S)	r(S−S)	angle (S−S=S)
S_4, C_{2v}	CBS(DTQ+d)	1.8948	2.1303	104.70
	expt	1.899(7)	2.173(32)	103.9(8)
	expt	1.898(5)	2.155(10)	104.2(2)
S_4, D_{2h}	CBS(DTQ=d)	*a*	2.5086	90.0

[a] Values did not follow an exponential fit.

6. Appendix

Modified cc-pVTZ basis set used for intial orbitals in QMC calculations, in GAMESS format.

```
S 13
1 374100.0000 0.5421400000E-04
2 56050.00000 0.4208550000E-03
3 12760.00000 0.2206980000E-02
4 3615.000000 0.9192580000E-02
5 1183.000000 0.3211230000E-01
6 428.8000000 0.9466830000E-01
7 167.8000000 0.2236300000
8 69.47000000 0.3743930000
9 29.84000000 0.3291080000
10 12.72000000 0.8470380000E-01
11 5.244000000 0.4408510000E-03
12 2.219000000 0.1648270000E-02
13 0.3490000000 0.3013060000E-03
S 13
1 374100.0000−0.1498370000E-04
2 56050.00000−0.1161980000E-03
3 12760.00000−0.6115830000E-03
4 3615.000000−0.2553700000E-02
5 1183.000000−0.9087080000E-02
6 428.8000000−0.2770450000E-01
7 167.8000000−0.7200200000E-01
8 69.47000000−0.1464390000
9 29.84000000−0.1951500000
10 12.72000000 0.8191930000E-02
11 5.244000000 0.5166010000
12 2.219000000 0.5421780000
13 0.3490000000−0.9180720000E-02
S 13
1 374100.0000 0.4350660000E-05
2 56050.00000 0.3371400000E-04
3 12760.00000 0.1776740000E-03
4 3615.000000 0.7411160000E-03
5 1183.000000 0.2645910000E-02
6 428.8000000 0.8074870000E-02
7 167.8000000 0.2122760000E-01
8 69.47000000 0.4383230000E-01
9 29.84000000 0.6127160000E-01
10 12.72000000−0.3615100000E-02
11 5.244000000−0.2045100000
12 2.219000000−0.3818710000
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13 0.3490000000 0.7141470000
S 1
1 0.7767000000 1.000000000
S 1
1 0.1322000000 1.000000000
P 7
1 574.4000000 0.2422640000E-02
2 135.8000000 0.1927960000E-01
3 43.19000000 0.8854010000E-01
4 15.87000000 0.2546540000
5 6.208000000 0.4339840000
6 2.483000000 0.3549530000
7 0.3229000000−0.5029770000E-02
P 7
1 574.4000000−0.6201020000E-03
2 135.8000000−0.4938820000E-02
3 43.19000000−0.2326470000E-01
4 15.87000000−0.6851950000E-01
5 6.208000000−0.1238960000
6 2.483000000−0.9694990000E-01
7 0.3229000000 0.5693940000
P 1
1 0.8688000000 1.000000000
P 1
1 0.1098000000 1.000000000
D 1
1 0.2690000000 1.000000000
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