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Fixed node diffusion Monte Carlo (FN-DMC) atomization energies are calculated for a benchmark set of 55 molecules. Using single determinant trial wave functions, comparison with experiment yields an average absolute deviation of 2.9 kcal/mol, placing this simplest form of FN-DMC roughly at the same level of accuracy as the CCSD(T)/aug-cc-pVQZ method. However, unlike perturbative wave function expansion approaches, FN-DMC is applicable to systems containing thousands of valence electrons. For the P_2 molecule, a number of possible sources of error are explored in detail. Results show that the main error is due to the fixed-node approximation and that this can be improved significantly with multireference trial wave functions. [DOI: 10.1063/1.1487829]

I. INTRODUCTION

Benchmark sets of molecules have proven to be a useful tool for gauging the accuracy and predictive abilities of a given computational method. A set of 31 molecules was originally grouped together to fit the semiempirical Gaussian-1 (G1) (Ref. 1) theory. This set, combined with 24 additional molecules containing second-row elements,[2] represents a broad range of chemical environments. The combined 55-molecule set, which we refer to here as the ''G1 set,'' is often used to test new theoretical methods. Computed G1 atomization energies for this set of molecules have a mean absolute deviation ϵ_{MAD} from experiment of 1.6 kcal/mol and a maximum deviation of 7.4 kcal/mol. These two numbers have become a standard benchmark for electronic structure approaches, including further G-n theories[3,4] as well as other state-of-the-art approaches such as the coupled cluster approximation with single, double, and perturbationally included triple excitations (CCSD(T)) (benchmark calculations, e.g., Refs. 5, 6), and density functional theory (DFT) methods (benchmark calculations, e.g., Refs. 7, 8).

Recently, the quantum Monte Carlo (QMC) approaches have been shown to provide highly accurate results when applied to a wide range of chemical systems (e.g., atoms, molecules, solids, nuclei, etc.) to calculate a wide range of properties (e.g., binding energies, reaction pathway energetics, optical gaps, momentum densities, etc.) (See, for example, Ref. 9 and references therein). A number of factors make QMC, which relies on a stochastic solution of the many-body Schrödinger equation, a highly attractive alternative to the more traditional mean-field and wave function expansion based techniques. Similar to the mean-field methods such as DFT, the computation time required in QMC scales as N^3 where N is the number of particles in the system. Yet, more closely related to post-Hartree–Fock wave function expansion methods, QMC solves the full $3N$-dimensional Schrödinger equation directly, allowing for explicit evaluation of electron correlation. Typically, within the diffusion Monte Carlo (DMC) variant the method recovers ~95% of the total valence correlation energy. Furthermore, very recent algorithmic developments have shown that QMC can be implemented to scale *linearly* as the number of particles, with effectively no loss of accuracy, by applying a unitary transform to localize the single-particle orbitals.[10] The combination of high accuracy and the ability to study systems with thousands of valence electrons makes QMC a very promising approach.

Despite the successes of QMC, comparisons with experiment have not been made systematically for a large data set, and the accuracy of QMC approaches has yet to be measured against a well-defined benchmark such as the G1 set. Recently, Manten and Lüchow have approached the subject of general accuracy for a small set of molecules and molecular reactions using all-electron fixed-node DMC,[11] and found accuracies for reaction energetics comparable to CCSD(T)/cc-pVTZ. Indeed, such studies are necessary and long overdue to answer many questions regarding the overall consistency and predictive capability of the approach. For example, when QMC is referred to as ''highly accurate,'' what exactly is meant? How big is the fixed-node error, on average? It is of great practical importance to answer these types of questions for a standard benchmark set of molecules such that one may better gauge the accuracy of QMC as well as develop further understanding of its limitations and methods for improvement.

In this work, results are presented for atomization energies calculated by single determinant, pseudopotential, fixed-node diffusion Monte Carlo (FN-DMC) for the 55 molecules in the G1 set. The average absolute deviation is 2.9 kcal/mol with a maximum deviation from experiment of 14 kcal/mol. These results support claims that QMC provides near ''chemical'' accuracy; however, it is also apparent that consistent accuracy of *less* than 1–2 kcal/mol is challenging within FN-DMC. Possible sources of error include: atomic orbital basis set, determinantal basis set, geometry, pseudopotentials, and zero-point energy. For the P_2 molecule, a detailed investigation of some of these potential sources of error has been carried out. Results show that one of the main sources of error is in the fixed node approximation which can be improved by including multiple determinants in the QMC trial wave function.

II. METHOD

In our QMC approach,[9,12–15] we use the variational Monte Carlo method to find an optimized correlated many-body trial function. This trial function is a product of Slater determinants and a correlation factor.[16] In the Slater determinant part, we employ natural orbitals (NO) rather than Hartree–Fock or density functional orbitals.[13] To eliminate most of the remaining variational bias we use the diffusion Monte Carlo method, which is based on the property that the operator $e^{-\tau H}$, where H is the Hamiltonian, projects out the ground state of any trial function with the same symmetry and nonzero overlap. All QMC results presented here are from the diffusion Monte Carlo approach.

Atomic cores are treated with Stevens–Basch–Krauss (SBK) effective core potentials[17] for all atoms except hydrogen, unless otherwise noted. The natural orbitals are derived from small multiconfiguration self-consistent field (MCSCF) calculations that include 15–30 virtual and all occupied valence orbitals in the active space.

FN-DMC calculations for all 55 molecules were carried out using a single determinant trial wave function except when noted. For multideterminant FN-DMC calculations, weights from MCSCF were used. In each case a single particle basis of quality similar to 6-311++G(2d,2p) was employed. More specifically, 3(4) uncontracted s and p functions, including 1 diffuse function, were used for first(second)-row elements. For all elements 2 uncontracted d functions were used. For the atomic part, contractions were generated from least squares fits of 6–12 Gaussians to the exact Hartree–Fock solution for the given pseudoatom.

Geometries were taken from the original G1 set,[1] i.e., optimized within MP2/6-31G(d). In order to make accurate comparisons with experiment, FN-DMC calculations were carried out for a long enough time to obtain stochastic error bars of <1 kcal/mol (typically 0.2–0.4 kcal/mol). Careful time-step studies were performed for several cases and conservative time steps were used for the entire set (i.e., DMC acceptance ratios were always greater than 99%).

All Hartree–Fock and MCSCF calculations in this work were performed using the GAMESS quantum chemistry package.[18] All LDA and GGA calculations were performed using the GAUSSIAN 98 program.[19]

III. RESULTS FOR THE G1 SET

The experimental data reported here are taken from a combination of NIST-JANAF tables[20] and Huber and Herberg,[21] in the same manner as Ref. 6. Experimentally measured atomization energies for the G1 set range from 17 kcal/mol (Na_2) to 709 kcal/mol (C_2H_2). Most experimental errors are small (i.e., <0.5 kcal/mol), although several are somewhat larger [e.g., CS has an experimental error of 6 kcal/mol (Ref. 20)]. To compare with theory, zero point energies are taken from experiment when available and from the calculations of Ref. 6 otherwise. For several species experimental errors are unavailable.

Calculated FN-DMC atomization energies for the 55 G1 molecules are shown in Table I. For each molecule, both the experimental and calculated binding energies are listed. Error bars are shown for experiment and theory (calculational error bars originate from the statistical sampling inherent in the DMC energy evaluation).

TABLE I. Atomization energies (kcal/mol) for the 55 molecules in the G1 set (Refs. 1, 2). Diffusion Monte Carlo (DMC) calculations and experimental (Expt.) results are listed. For DMC, statistical error bars are given in parentheses. Experimental errors are listed in parentheses (a dash indicates no error was available).

Molecule	DMC	Expt.
LiH	55.3(2)	56.00(1)
BeH	43.0(2)	46.90(1)
CH	79.5(2)	79.90(2)
CH_2 ($^3B_1$)	181.9(4)	179.6(4)
CH_2 ($^1A_1$)	169.7(4)	170.6(4)
CH_3	290.9(2)	289.3(2)
CH_4	395.0(2)	392.5(1)
NH	78.2(4)	79.0(4)
NH_2	169.2(4)	170.0(3)
NH_3	276.5(2)	276.7(1)
OH	101.2(3)	101.4(3)
H_2O	219.4(2)	219.35(1)
HF	135.9(2)	135.2(2)
SiH_2 ($^1A_1$)	145.5(2)	144.4(2)
SiH_2 ($^3B_1$)	125.8(2)	123.4(2)
SiH_3	215.1(2)	214(1)
SiH_4	305.8(2)	302.6(5)
PH_2	143.7(2)	144.7(6)
PH_3	224.8(2)	228.6(4)
H_2S	172.1(4)	173.1(2)
HCl	103.4(4)	102.2(5)
Li_2	23.5(2)	23.9(7)
LiF	145.1(4)	138(2)
C_2H_2	390.0(4)	386.9(2)
C_2H_4	533.5(4)	531.9(1)
C_2H_6	669.3(4)	666.3(-)
CN	170.5(4)	178(2)
HCN	302.0(8)	301(2)
CO	253.2(3)	256.2(2)
HCO	269.8(4)	270(2)
H_2CO	357.5(5)	357.2(1)
H_3COH	483.8(5)	480.8(-)
N_2	221.0(8)	225.1(4)
N_2H_4	406.8(9)	405.4(-)
NO	142.9(4)	150.06(4)
O_2	111.7(5)	117.96(2)
H_2O_2	246.6(3)	252.3(-)
F_2	32.0(8)	36.9(1)
CO_2	379.5(4)	381.93(1)
Na_2	17.3(2)	16.8(3)
Si_2	73.3(2)	74.0(-)
P_2	107.9(2)	116.1(5)
S_2	98.3(3)	100.66(7)
Cl_2	54.3(2)	57.18(1)
NaCl	98.8(3)	97.3(5)
SiO	186.7(2)	190(2)
CS	165.4(5)	169(6)
SO	117.6(6)	123.4(3)
ClO	55.4(4)	63.42(2)
ClF	53.7(6)	59.1(1)
Si_2H_6	505.8(4)	500.1(-)
CH_3Cl	371.6(8)	371.0(-)
H_3CSH	446.0(4)	445.1(-)
HOCl	152.8(4)	156.3(5)
SO_2	240.0(8)	254.0(2)

The largest error between FN-DMC and experiment oc-

curs for the SO_2 molecule, where the discrepancy is 14 kcal/mol. This makes SO_2 a somewhat special case as the next largest error in the set is only ~8 kcal/mol. The sensitivity of the atomization energy of SO_2 to the single particle basis has been studied carefully for the CCSD(T) approach.[6,22,23] In particular, it was found that SO_2 showed very slow convergence with respect to standard correlation consistent basis sets [e.g., CCSD(T)/aug-cc-pVQZ is 10 kcal/mol underbound], and that the addition of tight *d* and *f* functions on sulfur improved the convergence considerably. For the FN-DMC method employed here, additional tight *d* and *f* functions on sulfur in the generation of the trial function did not improve the energy. Because this molecule is somewhat larger and its error is so much greater than any other case, additional studies and ways for improving the FN-DMC result for SO_2 are relegated to a separate study.

After SO_2, the molecules with the biggest discrepancy from experiment are P_2, ClO, CN, LiF, and NO, with errors −8.2, −8.0, −7.6, +7.5, and −7.1 kcal/mol, respectively. Averaging over all molecules in the set yields a fairly good agreement between FN-DMC and experiment, with a mean absolute deviation of 2.9 kcal/mol (excluding SO_2 lowers this number to 2.5).

It is interesting to compare the FN-DMC results against other quantum chemical approaches. Previous studies have compared a number of DFT methods for the G1 test set, including local density approximation (LDA) and a variety of generalized gradient approximations (GGA).[7,8] As expected, LDA overbinds for every molecule in the set (except LiF), with ϵ_{MAD}~40 kcal/mol. The GGAs offer significant improvements over LDA, with the best functionals (B3LYP and B3PW91) giving ϵ_{MAD}~2.5 kcal/mol. It was shown that the key ingredient to achieving this result was in the 3-parameter B3 exchange function,[24] which uses a semiempirical fit to incorporate a fraction of the exact Hartree–Fock exchange. It was also noted that while ϵ_{MAD} for a larger 93-molecule test set using the same B3 functional was only 1 kcal/mol higher than for the original 55-molecule test set, the *maximum* deviation was doubled to 20 kcal/mol. This significantly larger range of error is evidence that accuracy trends in DFT methods are not always systematic and must be checked; a given functional working well for one problem does not necessarily imply it will work as well for another.

CCSD(T) has proven to be one of the most accurate *ab initio* electronic structure technique when applied with large basis sets to small molecules. Recent CCSD(T) calculations for atomization energies of the 55 G1 molecules provide a wealth of valuable information regarding the accuracy of CCSD(T).[5,6] It was found that CCSD(T)/aug-cc-pVQZ has ϵ_{MAD}=2.8 kcal/mol which is very similar to the FN-DMC results presented here. Using the CCSD(T) complete basis set limit, by extrapolating a series of correlation consistent basis sets, reduces ϵ_{MAD} by half to 1.3 kcal/mol. It would be interesting to attempt to formulate and apply such extrapolation techniques to FN-DMC, for example, using determinantal (rather than single particle) basis expansions.

Part of the advantage of having data for a benchmark set of molecules is the ability to look for trends within the set. There are several possible reasons for the errors in the present FN-DMC results (see discussion in next section), so it may be difficult to identify a single quantity or property that points to a trend. Indeed, as shown in Table II, a comparison of the 27 worst case molecules with the 28 best case ones does not seem to yield any visible trends for a number of properties; if anything, the trends appear to be counterintuitive. For example, one might expect closed-shell systems with large gaps to be, on average, better represented by a single Slater determinant. The results here show that while both subsets are mostly closed-shell in character, the better-performing half of the G1 set has more open-shell molecules, and the average gap over the closed shell cases is actually smaller than the same average over the worse half of the set. One might also guess that the weights of excited state determinants from MCSCF calculations may tend to be larger for the poorer performers (meaning that the true wave function is better represented with a multireference description). However, we find that the average weights are very similar, with only a very slight, essentially insignificant, difference (0.080 vs 0.075) between the two subsets.

TABLE II. FN-DMC error, FN-DMC ϵ_{MAD}, Hartree–Fock HOMO-LUMO gap, and two largest CSF weights from MCSCF calculations averaged over the 27 worst and 28 best FN-DMC energies in the G1 set. A breakdown of the kinds of spin multiplicities is also given, where S=singlet, D=doublet, and T=triplet.

	27 Worst	28 Best
ϵ_{avg} (kcal/mol)	−2.7	+0.2
ϵ_{MAD} (kcal/mol)	5.0	0.9
Spin multiplicities	20S, 4D, 3T	17S, 7D, 4T
HOMO-LUMO gap (eV)	14.4	11.6
Ground state CSF weight	0.959	0.964
Second largest CSF weight	0.080	0.075

It is also interesting to note that the average error among the worst 27 cases is negative at −2.7 kcal/mol, while the same average for the best 28 molecules is nearly zero at +0.2 kcal/mol. This difference may be indicative of the following general tendency. If FN-DMC fails to describe the atom and molecule with the same degree of accuracy, it is far more likely that the larger error will be made on the molecule.

IV. IMPROVEMENT OF THE P_2 MOLECULE

As mentioned, all of the FN-DMC results listed in Table I are obtained from trial wave functions using a single slater determinant built from natural orbitals. In order to probe the main source of discrepancy from experiment, one can examine how changes to this trial wavefunction impact the FN-DMC result. For such a study, we choose one of the worst case molecules, P_2, since its relatively small size allows for a number of thorough tests to be carried out.

A. Pseudopotentials

One possible source of error is due to the use of pseudopotentials. It is difficult to compare our pseudopotential DMC results with all-electron DMC calculations since the core electrons introduce additional nodal error which would be hard to separate from the effect of the pseudopotential.

TABLE III. DMC atomization energies (kcal/mol, with zero-point corrections) for the P_2 molecule calculated with two trial wave functions using three different pseudopotentials (PP).

Trial function	Hartree–Fock PP	LDA PP	BPW91 PP
LDA	108.9(2)	110.7(2)	107.9(3)
BPW91	108.9(2)	110.4(2)	107.8(3)

Although in this work the SBK (Ref. 17) pseudopotentials are employed, a number of other types of pseudopotentials are available. In addition to the method of construction, there are different theories on which the psuedopotential can be based. For example, SBK pseudopotentials are based on Hartree-Fock, but others can be made from LDA, GGA or other correlated theories.

When comparing different pseudopotentials for use in DMC calculations, if one remains consistent between pseudopotential and trial wave function there is little impact of the pseudopotential on the DMC result. For example, we compared two DMC calculations using Hartree–Fock trial functions with two different Hartree–Fock pseudopotentials, SBK and Hay–Wadt.[25] The DMC atomization energies for these cases were the same to within statistical error bars. On the other hand, if one were to construct a trial function generated by one method using a pseudopotential generated by a different method, there may be differences among the resulting DMC atomization energies. These differences are illustrated in Table III which lists DMC atomization energies based on single determinant trial functions generated using two different methods (LDA and GGA) and three different pseudopotentials (Hartree–Fock, LDA, and GGA) for each method.

Note that for LDA trial functions, the largest FN-DMC atomization energy is obtained with the LDA pseudopotential (i.e., the method used to construct the pseudopotential is the same as that used to build the trial function). However, for GGA trial functions, the largest atomization energy is not obtained with the GGA pseudopotential, but rather with the pseudopotential generated within LDA. In fact both the Hartree–Fock and LDA pseudopotentials give larger FN-DMC atomization energies than the GGA pseudopotential, for LDA or GGA trial functions. Table III indicates that, at least for this case, the FN-DMC atomization energy is more strongly dependent on the pseudopotential than on the method used to construct the trial wave function. This result is tested further below by comparing different trial functions all with the same pseudopotential.

Based on these results, it is likely that the FN-DMC error is partially due to an error in the pseudopotential. While it is difficult to quantify this error (making a comparison between pseudopotential and all-electron FN-DMC is somewhat ambiguous), we can nevertheless estimate that the error in FN-DMC due to the pseudopotential is roughly on the order of the differences observed in Table III, around 2 kcal/mol.

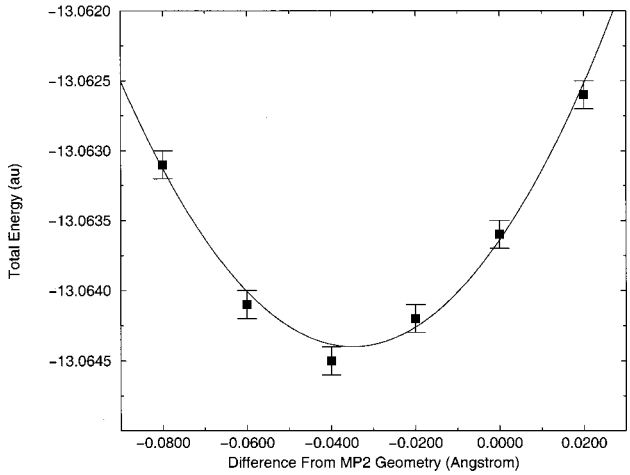

FIG. 1. FN-DMC energy of the P_2 molecule as a function of the bond distance. The solid line represents a quadratic fit to the QMC data. The x-axis has been shifted by the MP2/631G(d) bond distance.

B. Geometry

The impact of how the P_2 bond distance is optimized is another important test in our attempt to improve the energy. Forces are still challenging to evaluate within QMC, although there has been recent progress.[26,27] In the case of the P_2 dimer, only a single bond distance needs to be optimized which can be done easily with a series of total energy calculations. Figure 1 shows FN-DMC energies for the P_2 molecule at varying bond distances. Note that the optimal FN-DMC bond distance is 0.035 Å shorter than the MP2/6-31G(d) value. The difference in energy between these two structures is ~0.5 kcal/mol. This small difference indicates that the sensitivity of atomization energy to geometry is fairly minimal in this case and is not a large source of the error from experiment.

Since the geometry correction is an order of magnitude less than the missing binding energy, we focus on the quality of the nodal structure which is likely to have a far greater impact. The FN-DMC nodes are determined entirely by the nodes of the Slater determinant(s) which are constructed with single-body orbitals. There are a number of ways in which one can easily at least attempt to improve upon these nodes. First, the accuracy of the single-body orbitals may be improved by increasing the atomic orbital basis sets. Second, the orbitals themselves can be taken from any number of theories (i.e., Hartree–Fock, LDA, GGA, NO, etc.), some of which may lead to better nodes than others. Third, the determinantal basis can be expanded to include more than a single determinant.

C. Single-particle orbitals

For pseudopotential calculations, it is generally assumed that the fixed-node error is not effected much by the quality of the atomic orbital basis, as long as the basis is sufficient (i.e., 6-311G* quality or better). For P_2, 3 atomic orbital basis sets were tested: $17s17p2d/4s4p2d$, $27s27p3d/6s6p3d$, and $32s32p8d/8s8p4d$. Contractions for these basis sets were least squares fit to the orbitals of the

TABLE IV. Total single determinant FN-DMC energy (a.u.) of the P_2 molecule for different types of orbitals used to fill the Slater determinant.

Orbitals	Total energy
Hartree–Fock orbitals	−13.0628(1)
Natural orbitals	−13.0636(1)
LDA orbitals	−13.0652(1)
BPW91 orbitals	−13.0652(1)
B3LYP orbitals	−13.0651(1)

exact Hartree–Fock solution for the P pseudoatom. Uncontracted basis functions were chosen to optimize the energy of the Hartree–Fock dimer. For each case FN-DMC total energies were computed with statistical error bars less than 0.0001 a.u. All 3 basis sets give the same total energy within error bars, indicating the relative insensitivity of the nodes to the atomic orbital basis in this case. It may be interesting to carry out this same kind of test systematically for other molecules in the set, although that is beyond the scope of the present work. Further, these atomic orbital basis set tests were performed with single determinant trial functions; it is possible that the effect of the atomic orbital basis becomes more important as the trial function is expanded to include multiple determinants.

A number of different single-particle orbitals have been used in the past to construct the Slater determinant part of QMC trial wave functions. In some cases, it was found that NO offer a slight improvement in the nodes over Hartree–Fock orbitals.[13] Other times, DFT orbitals may be more appropriate. It is difficult to predict *a priori* which orbitals are better suited to a given system. In many cases, the resulting differences tend to be rather small. Table IV lists the total energy of the P_2 molecule using a single Slater determinant built from five different kinds of orbitals: Hartree–Fock, NO, LDA, BPW91, and B3LYP. The same Hartree–Fock SBK pseudopotential was used in each case. Note that using the NO gives a small (~0.7 kcal/mol) improvement over Hartree–Fock, and the LDA and GGA orbitals are slightly better (~1.0 kcal/mol) than NO. While it is interesting that in this case the DFT orbitals are best, they only account for 1 of the 8 kcal/mol FN-DMC error found with NO. Of course, other single-body orbitals could be used, however it appears that, like geometry, the choice of single-body orbitals is a small contribution to the discrepancy with experiment.

D. Multiple determinants

Another way to change and possibly improve the nodal surface of the trial QMC wave function is to use more than a single Slater determinant. Just as an expansion of the determinantal basis increases the variational freedom in the wave function and therefore lowers the total energy in post-Hartree–Fock calculations, multideterminantal trial wave functions can lead to better nodes which lower the FN-DMC total energy.[28] In general, however, a given determinantal expansion that improves the variational energy does not always lead to a similar improvement in the nodal surface. In fact, recent work has shown that MCSCF-based trial functions may not improve the FN-DMC energy[29] and in some cases can even worsen the fixed node error.[30] It has also been suggested recently that multideterminantal trial functions based on pair natural orbital CI wave functions may improve the nodal surface more efficiently than MCSCF-based trial functions.[31]

TABLE V. Total FN-DMC energy (a.u.) of the P_2 molecule with differing number of determinants in the trial wave function. The number of virtual states in the MCSCF calculation is also listed. For each case, all configuration state functions with weight greater than 0.01 were included.

No. of determinants	No. virtual states	Total energy
1	1	−13.0628(1)
54	3	−13.0660(1)
167	8	−13.0696(1)
269	16	−13.0701(1)
245	25	−13.0691(1)
223	40	−13.0698(1)

Table V shows the total FN-DMC energies for P_2 using several different multireference trial functions. In each case, determinants were taken from a MCSCF calculation in which all occupied electrons were singly and doubly excited into a given number of virtual states. The number of resulting determinants corresponds to a threshold of 0.01 for the weight of the configuration state functions (CSF) to keep. Weights of these determinants in the FN-DMC calculations are taken to be the same as the MCSCF weights. Of course, these weights may not be ideal since they are taken from a minimization of the total energy which may not always correspond to improving the nodal surface. Nonetheless, MCSCF weights provide a good starting point and can help guide us in selecting the determinants.

Note that the energies are improved using a multireference trial function based on MCSCF orbitals and weights. Using a single determinant of MCSCF orbitals gives the same FN-DMC energy as Hartree–Fock orbitals, slightly higher than the NO single determinant energy (see Table IV). Taking excitations into just the first three virtual states lowers the FN-DMC energy by 2.1 kcal/mol compared with a single determinant.

In going from 3 to 8 virtual states in the MCSCF calculation, the FN-DMC energy is improved yet again rather substantially. With a 167-determinant wave function, the FN-DMC energy is 4.3 kcal/mol lower in energy than a single determinant. The additional improvement may be due to the fact that the 167-determinant expansion includes excitations into *d*-like orbitals not present in the smaller 54-determinant run. This explanation is in good agreement with previous work which found that significant improvement in the nodal structure of several atoms[32] and the N_2 molecule[33] relied on the inclusion of determinants with excitations into *d* states.

The largest determinantal expansion listed is for 269 determinants from a MCSCF calculation that included excitations into 16 virtual states. The energy for this case is only slightly improved [0.3(1) kcal/mol] compared to the 167-determinant case. This makes our best multideterminant FN-DMC energy roughly 4.1(1) kcal/mol lower than the single-determinant NO result listed in Table I.

Further excitations into more virtual states in the MC-

SCF calculations do not lead to further improvements in the FN-DMC energy. This may be partly due to the fact that we use here the same cutoff (0.01) for the CSF weights in all cases. As the number of virtual states increases, the total number of determinants increases and the weights of each determinant decrease. (This is also the reason why the number of determinants decreases for the last two rows of Table V.) Such an explanation cannot be complete, however, since the energy is improved in going from 25 to 40 virtual states (245 to 223 determinants).

We have so far only examined the improvement in total energy of the P_2 molecule. Of course, to compute the atomization energy one must also know the energy of the P atom. Therefore, it is reasonable that if multireference determinants are used for the molecule one should recompute the atomization energy using a similar multideterminant wave function for the atom. A 66-determinant trial function for the P atom was generated from a MCSCF calculation with excitations into 24 virtual states. The energy was indeed lower than the single determinant FN-DMC energy, but only by 0.3(1) kcal/mol. The best correction above, then, is 3.5 kcal/mol when referring to the atomization energy.

In our quest to improve the FN-DMC atomization of the P_2 molecule, we have found ~2.0 kcal/mol (pseudopotential), 0.5 kcal/mol (geometry), 1.0 kcal/mol (single-body orbitals), and 3.5 kcal/mol (determinantal basis). Previous work[6] found roughly 0.8 kcal/mol in core-valence correlation (not included here due to our use of pseudopotentials) and a 0.2 kcal/mol correction due to scalar relativistic effects. A sum of these individual effects would result in a 8.0 kcal/mol improvement in the atomization energy of P_2, bringing the error with experiment to -0.2 kcal/mol. Although it is not entirely clear that one can sum these errors (i.e., that the correction terms listed above are unrelated) it is nonetheless evident that a substantial improvement can be made in this case.

Another, somewhat complicated source of error is the localization error[11] which is intimately connected with the fixed-node error. It was shown that the localization error scales as the error in the trial function squared.[11] Thus, with a good enough trial function, it is typically assumed that this error is minimal (i.e., significantly smaller than the statistical error bars). However, in the current set of data we are exploring small energies with very small error bars.

It is likely that the 4.1 kcal/mol improvement found by expanding the determinantal basis is an improvement in *both* the nodal error and the localization error. To separate the two is, unfortunately, exceedingly difficult, particularly since improving the nodes also improves the localization error. Figure 2 shows the total energy of the P_2 molecule as a function of the number of determinants for two trial functions: one with the full Jastrow as used throughout this work, and one without any Jastrow term. For a given number of determinants, the nodal surface is the same in both cases. For one determinant, the difference between the two curves is entirely due to the localization error. However, as the number of determinants is increased, the nodal error is improved which in turn improves the locality error and separating the two is not possible. For the purpose of this discussion, when referring to the fixed-node error we mean more precisely a combination of fixed-node and localization errors.

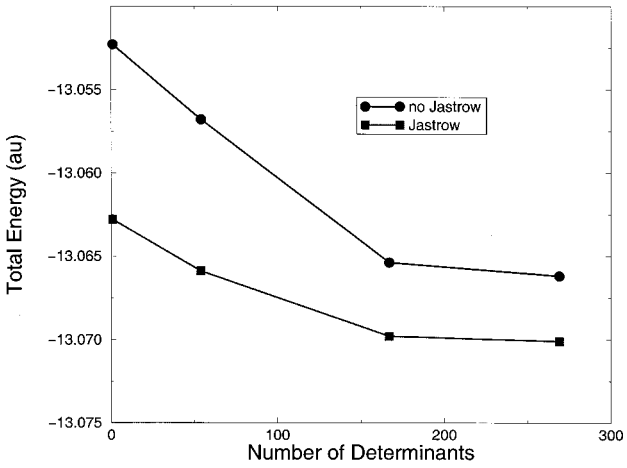

FIG. 2. FN-DMC energy of the P_2 molecule as a function of the number of determinants in the trial function. Results both with and without a Jastrow function are shown. Statistical error bars are smaller than the symbols shown.

V. CONCLUSIONS

The accuracy of the pseudopotential FN-DMC approach has been assessed for the 55 G1 molecules. For these calculations, the method was treated in as ''black box'' a way as possible. For example, all calculations were run systematically with the same basis sets and type of orbital for a single determinant trial function. With such an approach, a mean absolute deviation of 2.9 kcal/mol was achieved. The main source of error for the P_2 molecule was found in the fixed-node approximation, a second important error was in the use of the SBK pseudopotential, and smaller errors were due to geometry and choice of single-body orbitals. The nodes were shown to be substantially improved by using multiple determinants in the trial function. These results indicate that ϵ_{MAD} could be significantly reduced (i.e., by a factor of 2) if multireference trial wave functions were employed for the whole set.

Many more careful studies are needed to understand the best means of improving the fixed-node error. It is our hope that the benchmark results provided in this work will aid in some of these studies. For example, the 5 or 10 worst case molecules could provide a useful laboratory for tests and improvements. Furthermore, the results presented here put pseudopotential single determinant FN-DMC on the map as a benchmark, with its absolute mean deviation now a number that can be directly compared with other methods.

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