

Quantum Monte Carlo Methods Describe Noncovalent Interactions with Subchemical Accuracy

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S Supporting Information

ABSTRACT: An accurate description of noncovalent interaction energies is one of the most challenging tasks in computational chemistry. To date, nonempirical CCSD(T)/CBS has been used as a benchmark reference. However, its practical use is limited due to the rapid growth of its computational cost with the system complexity. Here, we show that the fixed-node diffusion Monte Carlo (FN-DMC) method with a more favorable scaling is capable of reaching the CCSD(T)/CBS within subchemical accuracy (<0.1 kcal/mol) on a testing set of six small noncovalent complexes including the water dimer. In benzene/water, benzene/methane, and the T-shape benzene dimer, FN-DMC provides interaction energies that agree within 0.25 kcal/mol with the best available CCSD(T)/CBS estimates. The demonstrated predictive power of FN-DMC therefore provides new opportunities for studies of the vast and important class of medium/large noncovalent complexes.



INTRODUCTION

Noncovalent molecular interactions play a key role in biology, materials science, and many areas of chemistry. Their most important manifestations are probably the molecular recognition, structure, and function of biomacromolecules, as well as the properties of liquids.^{1,2} In general, experiments may provide information on the strength of noncovalent interactions (e.g., dissociation enthalpies D_0 , adsorption enthalpies, etc.), but direct information on their nature is not available. A combination of multiple methods^{3,4} is thus required for their precise characterization. In addition to experiments, complementary and independent information necessary for fundamental understanding of noncovalent interactions is therefore provided by the theory and high-accuracy calculations. Since the binding energies of noncovalent complexes are weak, typically ranging from 0.5 to 30 kcal/mol (for small complexes), their computations need methods of exceptional quality, well beyond the traditional chemical accuracy of 1 kcal/mol. For that reason, only energy differences at subchemical accuracy,⁵ i.e., with an error of less than 0.1 kcal/mol, are considered accurate enough. Reaching this level of accuracy is one of the most challenging tasks in modern computational chemistry.

Currently, the CCSD(T)⁶ (coupled-cluster singles and doubles with noniterative triples) method has been established as the “gold standard” of the quantum mechanical calculations of noncovalent interactions.⁷ It is frequently considered as a benchmark that guarantees the desired accuracy for interaction energies, provided that large enough basis sets and/or complete basis set (CBS) extrapolations are employed. Recently, the accuracy of the CCSD(T)/CBS calculations for small noncovalent complexes with up to 12 atoms has been analyzed in detail, and the errors coming from the approximations involved (frozen core and Born–Oppenheimer approximations, the neglect of relativistic effects, and incomplete excitation expansion) have been estimated.^{8,9} The errors caused by these approximations were surprisingly small ($\approx 1.5\%$ of the interaction energies on average), and this favorable conclusion was attributed to the systematic error cancellation in energy differences. The reported analysis clearly demonstrates that, in *small complexes*, CCSD(T) has been able to reach subchemical accuracy. In large complexes, the accuracy of this approach still remains to be verified, because of the rapid growth of computations, $\propto O(N^7)$, with the basis-set size and even more

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steeply growing demands of higher order approaches such as CCSDT(Q), necessary for ascertaining the genuine accuracy of the CCSD(T) level.⁸

One of the promising alternatives for solving the electronic nonrelativistic Schrödinger equation in Born–Oppenheimer approximation is the fixed-node (FN) diffusion Monte Carlo (DMC/FN-DMC) method, a member of the quantum Monte Carlo (QMC) class of the explicitly correlated many-body methods based on random sampling.^{10,11} The FN-DMC approach is mostly used for its direct treatment of many-body correlations,^{10,11} favorable low-order polynomial scaling, $\propto O(N^{3-4})$,¹⁰ with the number of electrons and *intrinsic* massive parallelism.^{10,11} The stochastic nature of QMC, i.e., representation of a wave function as an ensemble of walkers (electron position vectors), results in energies that are much less sensitive to basis-set superposition errors and reach the CBS-equivalent regime easily.¹¹ Furthermore, it allows one to sample sophisticated many-body wave function ansätze with explicit interelectronic dependencies very efficiently.^{10–13} QMC has its own disadvantages such as slowly convergent error bars intrinsic to stochastic sampling, the necessity to circumvent difficulties in sampling electronic wave functions which are not positive everywhere, and complications in the estimations of quantities beyond energies. Despite this, QMC approaches are behind some of the most paradigmatic results obtained for quantum systems such as the correlation energy of electron gas,¹⁴ which is widely used in many electronic structure methods in physics and chemistry.

The DMC method is based on the imaginary time projection of the ground state from an appropriate trial wave function.^{10,11} Since the DMC solution of the stationary Schrödinger equation is represented as a stochastic density of walkers that must be positive everywhere, the well-known “sign problem” emerges due to the antisymmetry of the electronic wave function. This can be overcome by the FN approximation, in which the node (the hyper-surface where the wave function vanishes) of the best available trial function is used to govern the electron-position sampling. This additional constraint unavoidably introduces a FN bias. Nevertheless, simple trial functions often recover a remarkably large amount of correlation energy (90–95%),¹⁰ and trial functions based on approaches such as Hartree–Fock (HF), post-HF, and density functional theory (DFT) have been successfully employed in a plethora of applications.^{10,14–24} Numerous examples show that FN-DMC is able to reach high (often chemical) accuracy^{11,22,23,25–27} and thus is competitive with the most accurate quantum chemical methods.^{17,22} Furthermore, the FN-DMC solution is systematically improvable, e.g., by including multiple determinants, by employing pair orbital antisymmetric forms, and/or by extensive variational Monte Carlo (VMC) optimizations of parameters that tune the nodes. Since the difference between the fixed-node and exact energies is proportional to the square of the discrepancy between the trial and exact nodes,¹⁰ the quality of the trial nodes determines the accuracy of the obtained total energies. For high-accuracy calculations, it is therefore worthwhile and necessary to benchmark the nodal biases and their impact on energy differences and other quantities. For more details and the rigorous background on QMC, see, e.g., refs 10, 11, and 13.

For noncovalent complexes, there are two especially salient features of FN-DMC. First, the method accurately describes the dynamical correlation effects crucial for noncovalent interactions, as FN-DMC recovers *all possible many-body correlations*

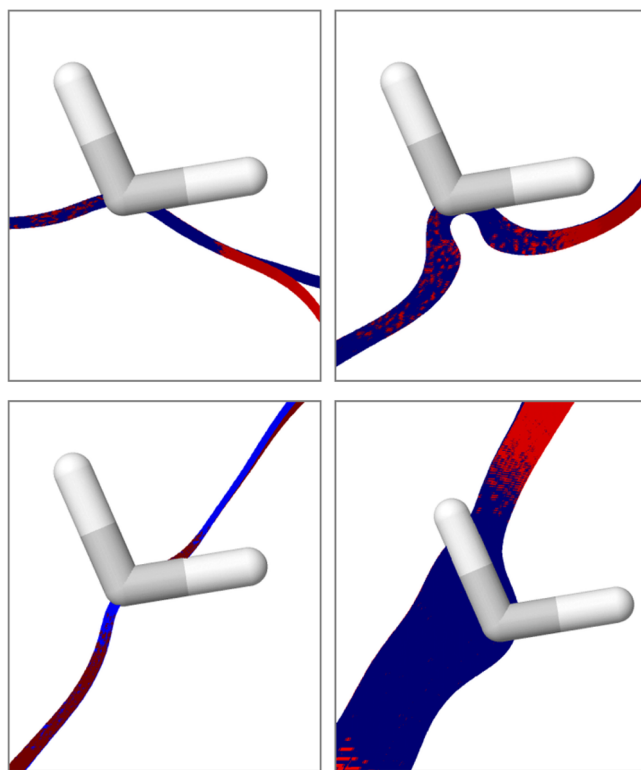


Figure 1. Four representative comparisons of the cuts through the multidimensional nodal hyper-surfaces ($\Psi = 0$) of the B3LYP/aug-TZV trial wave functions Ψ for the water dimer complex (blue, only one molecule is zoomed in) and isolated water molecule in the same position as the one in the dimer (red). In each of the four independent pictures, the produced blue and red 2D ribbon-like single-electron scans (for more details, see Methods) are essentially indistinguishable in the region of the monomer where the electron density achieves its maximum, providing thus visual rationalization of the FN error cancellation observed in weakly interacting molecular complexes.

within the given nodal constraint. Second, the finite FN error in DMC is expected to cancel out nearly exactly^{26,28,29} in energy differences, since the nodes in the region of the molecule A are essentially unchanged by the presence of the weakly interacting molecule B and vice versa. This trend is indeed qualitatively confirmed by the direct inspection of the nodal surfaces (Figure 1). Whenever strong multireference effects such as low-lying near-degeneracies are absent, straightforward single-determinant trial functions (e.g., based on DFT orbitals) are expected to suffice. For these reasons, FN-DMC was found to be very promising in treating medium/large molecular systems,^{24,30,31} where conventional correlated methods were inapplicable due to the prohibitive computational cost. Therefore, one of the key motivations of our study is whether this approach can reach subchemical accuracy in noncovalent complexes. Note that this is an accuracy 1 order of magnitude higher than the typically expected accuracy of QMC.

Considering the importance of noncovalent interactions and the potential of QMC, relatively few applications have been presented so far, see e.g. refs 26–38. In many cases, the approaches appear too technical or costly for routine use,^{34,35} or the desirable systematic agreement with CCSD(T) results, even in small systems, is not satisfactory.^{26,29,37} Taking the proven reliability of CCSD(T) interaction energies in small complexes into account,⁸ accurate QMC calculations can be cross-validated with these results. In the present work, we show

that FN-DMC with single-determinant trial functions is able to approach the CCSD(T)/CBS reference to within 0.1 kcal/mol (one standard deviation errors are reported) for small complexes. In addition, the identified easy-to-use protocol is tested on larger complexes, where the reliability of CCSD(T) has yet to be fully tested. Here, the final FN-DMC results agree to within 0.25 kcal/mol with the best available estimates. These results show the potential of QMC for reliable estimation of noncovalent molecular interaction energies well below chemical accuracy.

The calculations were performed on a diverse set of hydrogen and/or dispersion bound complexes for which reliable estimates of interaction energies already exist^{8,39,40} and which were previously studied within QMC.^{26,29,34,35} The considered test set consists of the dimers of ammonia, water, hydrogen fluoride, methane, ethene, and the ethene/ethyne complex (Figure 2). The larger considered complexes include benzene/methane, benzene/water, and T-shape benzene dimer (Figure 2).

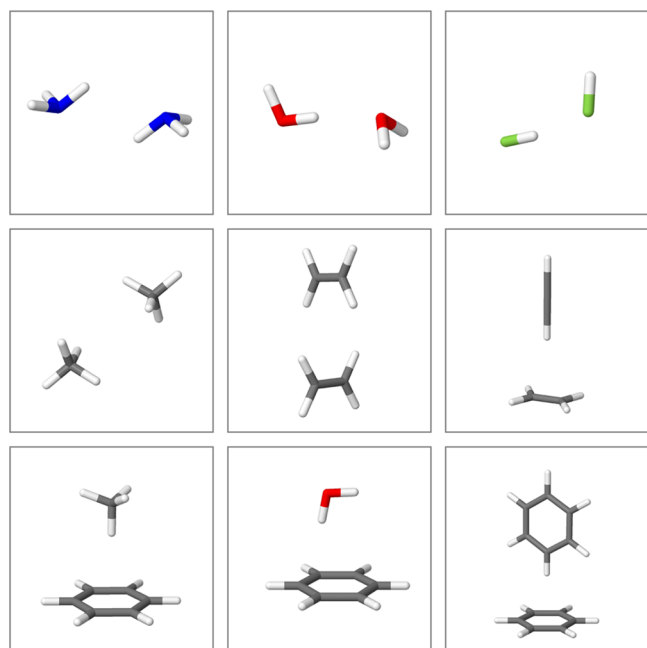


Figure 2. The set of molecules used in the present work (from top left, to bottom right): ammonia dimer, water dimer, hydrogen fluoride dimer, methane dimer, ethene dimer, and the complexes of ethene/ethyne, benzene/methane, benzene/water, and benzene dimer T-shape.

■ ADJUSTING THE QMC PROTOCOL

The present methodology was developed via extensive testing and elimination of the biases that affect the final FN-DMC energies. Clearly, this has to be done in a step-by-step manner since several sets of parameters enter the multistage refinement strategy^{16,21} on the way to the final FN-DMC results. The sequence of the steps includes (i) the construction of the trial wave function, (ii) its VMC optimization, and (iii) FN-DMC production calculation. The tasks i and ii involve optimizations which affect the final interaction energies obtained in iii as the differences of the statistically independent total energies.

We employ trial wave functions of the Slater–Jastrow type,^{10,11} in general, a product of the sum of determinants

and a positive definite Jastrow term¹² explicitly describing the interparticle correlations. Remarkably, we have found that single-reference wave functions filled with B3LYP/aug-TZV orbitals reach the desired accuracy criterion for the whole test set; consequently, multiple determinants were not considered. Orbital sets from other methods were mostly comparable; in the ammonia dimer complex, for instance, the HF nodes provide the same FN-DMC interaction energy as B3LYP (-3.12 ± 0.07 vs -3.10 ± 0.06 kcal/mol) within the error bars, due to the FN error cancellation^{26,28,29} (cf. Figure 1). Nevertheless, the total energies from B3LYP orbitals were found to be variationally lower than those from HF (in dimer by ~ 0.001 au), in agreement with previous experience.^{15,41} Regarding the one-electron basis set, tests on the ammonia dimer confirm the crucial effect of augmentation functions (cf. ref 29). For the same system, TZV and QZV bases result in interaction energies of -3.33 ± 0.07 and -3.47 ± 0.07 , whereas the aug-TZV and aug-QZV bases give -3.10 ± 0.06 and -3.13 ± 0.6 kcal/mol, so that the impact of augmentation is clearly visible and in accord with the reference value of -3.15 kcal/mol.⁴⁰ On the other hand, the increase of basis set cardinality beyond the TZV level plays a smaller role than in the mainstream correlated wave function methods.

In order to reduce the numerical cost of the calculations, effective core potentials (ECP) were employed for all elements (cf. Methods). Typically, this causes a mild dependence of the FN-DMC total energy on the Jastrow factor,^{42,43} which cancels out in energy differences with an accuracy ≈ 1 kcal/mol. In our systems, elimination of this source of bias requires fully converged Jastrow factors including electron–electron, electron–nucleus, and electron–electron–nucleus terms so as to keep the target of 0.1 kcal/mol margin in energy differences. This is true except for the water dimer, where a standard Jastrow factor produces inaccurate energy difference (-5.26 ± 0.09 kcal/mol, cf. Table 1), and a distinct Jastrow factor including unique parameter sets for nonequivalent atoms of the same type is required.⁴⁴ For the sake of completeness, we note that the model of ammonia dimer, taken from the S22 set,³⁹ is not a genuine hydrogen bonded case, where the same behavior would be expected, but a symmetrized transition structure that apparently does not require more parameters in the Jastrow factor. Note that a more economic variant of the correlation factor, with only electron–electron and electron–nucleus terms, doubles the average error on the considered test set, and therefore it would be inadequate for our purposes.⁴⁴ The parameters of the Jastrow factor were exhaustively optimized for each complex and its constituents separately, using a linear combination of energy and variance cost function.⁴⁵ We have found that for large complexes, 7–10 iterations of VMC optimization are sometimes necessary to reach the full convergence.

The production protocol thus consists of (i) Slater–Jastrow trial wave functions of B3LYP/aug-TZV quality, (ii) a converged VMC optimization of the Jastrow factor with electron–electron, electron–nucleus, and electron–electron–nucleus terms, and (iii) a FN-DMC ground-state projection using the T-moves scheme⁴³ and a time step of 0.005 au. Note that the VMC reoptimization of orbitals has not been explored, although it could be tested in the future as well. The error bars were converged to at least ~ 0.1 kcal/mol in the projection time of several thousands of atomic units.

Table 1. Calculated FN-DMC Interaction Energies (kcal/mol), Based on B3LYP/aug-TZV Guiding Functions, Compared to the Previous FN-DMC²⁶ and Reference CCSD(T)/CBS Data^{8,40} Together with the Corresponding Differences Δ^a

complex	reference	FN-DMC ^b	Δ^b	FN-DMC ^c	Δ^c
ammonia dimer	−3.15	−3.19 ± 0.09	0.04	−3.10 ± 0.06	−0.05
water dimer	−5.07	−5.34 ± 0.09	0.27	−5.15 ± 0.08	0.08
hydrogen fluoride dimer	−4.58			−4.68 ± 0.10	0.10
methane dimer	−0.53	−0.48 ± 0.08	−0.05	−0.44 ± 0.05	−0.09
ethene dimer	−1.48	−1.38 ± 0.13	−0.10	−1.47 ± 0.09	−0.01
ethene/ethyne	−1.50	−1.22 ± 0.12	−0.28	−1.56 ± 0.08	0.06
benzene/water	−3.29	−3.69 ± 0.24	0.40	−3.53 ± 0.13	0.24
benzene/methane	−1.45	−0.63 ± 0.21	−0.87	−1.30 ± 0.13	−0.15
benzene dimer T	−2.71	−3.77 ± 0.39	1.06	−2.88 ± 0.16	0.17

^aThe reference values for the test set (the top panel) are obtained by extrapolation of CCSD(T) (aug-TZV, aug-QZV) to the CBS limit, while for larger complexes (the bottom panel), the estimates combine contributions from MP2/CBS (aug-TZV, aug-QZV) and CCSD(T)/CBS (aug-DZV, aug-TZV). ^bKörth et al.²⁶ ^cThis work.

RESULTS AND DISCUSSION

The production FN-DMC results compared to the previous FN-DMC data²⁶ and the reference CCSD(T)/CBS data^{8,40} are reported in Table 1. We note that in all complexes from the test set, the statistical and systematic errors of our results with respect to the reference are ~ 0.1 kcal/mol or better, which is a remarkable achievement. Here, the mean error (ME) and mean unsigned error (MUE) are found to be -0.002 and 0.058 kcal/mol, respectively, and the relative error (RE) remains below 5%. For comparison, the ME/MUE of FN-DMC results obtained by Körth et al.²⁶ (the same set of values is compared) amount to $-0.024/0.148$ kcal/mol (RE: 6.2%) indicating that our QMC protocol provides lower MUE. The situation is even more marked when it comes to larger complexes, where the previous ME/MUE amounts to $0.213/0.760$ kcal/mol (RE: 35.9%); whereas we achieve $0.087/0.187$ kcal/mol (RE: 8.2%), i.e., much smaller average MUE and RE. Especially encouraging is the result obtained for the largest considered system, the benzene dimer, where the previous attempt²⁶ was found to differ from the CCSD(T)/CBS reference by more than 1 kcal/mol (Table 1).

The difference between our values and previous FN-DMC data²⁶ probably comes from different trial wave functions, the different cost function used in VMC optimizations, and the different number of Jastrow factor optimization steps. Our trial wave functions are constructed using an augmented TZV basis, which appears to provide more consistent interaction energies than nonaugmented QZV basis set used in ref 26. In larger molecules, it is also possible that the Jastrow factor is not fully converged after three VMC optimization iterations used.²⁶ In the case of the water molecule, we find that a distinct Jastrow factor (discussed above) must be used to reach the 0.1 kcal/mol accuracy. Finally, the variance used as a cost function in the VMC optimization of trial functions leads to higher FN-DMC total energies, as compared to the energy minimization (we use 95% of energy and 5% of variance, cf. Methods).⁴⁵

The high level of accuracy achieved with relatively simple trial functions may be primarily attributed to the consistent FN error cancellation,²⁸ which takes place for two reasons. The molecular complex constituents interact weakly; i.e., the interactions do not perturb the nodes of the constituents (Figure 1). Furthermore, since the constituent monomers are closed-shell in nature, the interaction energy is dominated by purely dynamic correlation. In contrast, the calculation of atomization energies of covalently bonded systems requires a

balanced description of both static and dynamic correlations so as to properly describe near degeneracies in isolated atoms and/or molecules. In such cases, errors of a few kilocalories per mole are not ruled out, and their elimination requires further efforts.⁴⁶

CONCLUSIONS

In summary, the FN-DMC method with an optimized protocol was found to provide reliable noncovalent interaction energy estimates. On a test set of six small complexes, with interaction energies ranging from 0.53 to 5.07 kcal/mol, the FN-DMC results agree to subchemical accuracy with the reliable benchmark CCSD(T)/CBS data. We believe that our results have important implications in several aspects. First, the results show that both types of QMC errors, *systematic and statistical*, can be an order of magnitude smaller than the typical ones obtained by the present day QMC methodology. Second, we have found an almost perfect cancellation of the fixed-node errors, between the closed-shell wave functions of the studied complexes and their constituents. This indirectly confirms that the corresponding many-body correlations are almost exclusively dynamical and are therefore fully captured by QMC. Third, our results for larger systems represent new and independent estimations of interaction energies with predictive power on par with the established coupled-cluster methodology. Since the scaling of QMC is more favorable than in traditional correlated methods and the number of the systems which could be possibly treated by the presented approach is high, we believe that our study opens promising new opportunities in the quest for an accurate and reliable description of noncovalently bound complexes.

METHODS

The geometries of the studied complexes were taken from the S22 set³⁹ except for the hydrogen fluoride dimer taken from the A25 set.⁸ ECPs with the corresponding basis sets by Burkatzki et al.⁴⁷ were used throughout the work, with the exception of the H, where a more accurate version was used.⁴⁸ Augmentation functions were taken from the corresponding Dunning bases.⁴⁹ Single-determinant trial wave functions of the Slater–Jastrow¹² type were constructed using B3LYP orbitals (GAMESS code⁵⁰). The Schmidt–Moskowitz⁵¹ Jastrow factor,¹² including the electron–electron, electron–nucleus, and electron–electron–nucleus terms, was expanded in polynomial Padé functions.¹³ The parameters of the Jastrow

factor were optimized by the Hessian driven VMC optimization of at least 10×10 iterations (i.e., a full VMC energy calculation after each 10 optimization steps on a fixed population), using a linear combination of energy (95%) and variance (5%) as a cost function.⁴⁵ These trial wave functions were used in the production FN-DMC runs performed with the conservative time-step of 0.005 au and the T-moves modification for the sampling of ECPs⁴³ that guarantees the variational property of total energies. The target walker populations ranged from 5000 (for small systems) up to about 20 000 (for the largest system).

The comparisons of the nodal hyper-surfaces for the water dimer (Figure 1) were produced by single-electron scans of a 3D volume, keeping the remaining $N - 1$ electron positions fixed in both dimer and monomer alike. Furthermore, the monomer scans used a subset of the dimer electron positions to produce comparable surfaces. Since the nodes exhibit rather complicated folds, representative nodal cuts were performed in a cuboid squeezed in one dimension so that the corresponding plots appear as ribbon-like.

All QMC calculations and data generation for the plots (Figure 1) were performed using the code QWalk.⁵²

■ ASSOCIATED CONTENT

● Supporting Information

Total energies related to the interaction energies reported in Table 1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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