

Influence of single particle orbital sets and configuration selection on multideterminant wavefunctions in quantum Monte Carlo

Raymond C. Clay III

*University of Illinois, Urbana, Illinois USA 61821 and
Lawrence Livermore National Laboratory,
7000 East Avenue, Livermore, California 94550, U.S.A.*

Miguel A. Morales*

*Lawrence Livermore National Laboratory,
7000 East Avenue, Livermore, California 94550, U.S.A.*

Abstract

Multideterminant wavefunctions, while having a long history in quantum chemistry, are increasingly being used in highly-accurate quantum Monte Carlo calculations. Since the accuracy of QMC is ultimately limited by the quality of the trial wavefunction, multi-Slater determinants wavefunctions offer an attractive alternative to Slater-Jastrow and more sophisticated wavefunction ansatzs for several reasons. They can be efficiently calculated, straightforwardly optimized, and systematically improved by increasing the number of included determinants. In spite of their potential, however, the convergence properties of multi-Slater determinant wavefunctions with respect to orbital set choice and excited determinant selection are poorly understood, which hinders the application of these wavefunctions to large systems and solids. In this paper, by performing QMC calculations on the equilibrium and stretched carbon dimer, we find that convergence of the recovered correlation energy with respect to number of determinants can depend quite strongly on basis set and determinant selection methods, especially where there is strong correlation. We demonstrate that properly chosen orbital sets and determinant selection techniques from quantum chemistry methods can dramatically reduce the required number of determinants (and thus the computational cost) to reach a given accuracy, which we argue shows clear need for an automatic QMC-only method for selecting determinants and generating optimal orbital sets.

*Electronic address: moralessilva2@llnl.gov

I. INTRODUCTION

The use of computational methods in the study of material properties has dramatically increased over the last decade, due in part to the success of mean-field methods like density functional theory (DFT). By approximately treating electronic correlation effects through an "exchange-correlation functional", DFT offers an excellent ratio between cost and accuracy, leading to its current position as the main workhorse in electronic structure and first-principles simulations. However, for systems that require a very accurate description of electronic correlation, improving the exchange-correlation functional is nontrivial and far from systematic, making highly accurate many-body methods increasingly attractive as computational resources exponentially increase.

Of these many-body methods, projector Quantum Monte Carlo (p-QMC) [1, 2] is especially attractive due to its high accuracy and modest computational cost, which it achieves through stochastically projecting and sampling the ground-state wavefunction of Schrödinger's equation. The fundamental limitation on the accuracy of projector QMC methods for realistic systems is the "fixed-node approximation". Here, one *assumes* that the nodes of the many-body ground-state wavefunction Ψ_0 are identical to those of an antisymmetric trial wavefunction Ψ_T . The p-QMC algorithm then projects out the lowest energy fermionic ground-state consistent with these boundary-conditions in polynomial time, in contrast to the exact algorithm which suffers from the "fermion sign-problem" and associated exponential scaling.

In standard-practices QMC, the nodes of the many-body wavefunction are taken to be equivalent to those of a single Slater determinant, built up from single-particle orbitals taken from a mean field theory like Hartree-Fock or density functional theory. Despite the simplicity of this nodal ansatz, experience dictates that this approximation is exceptionally good at capturing the majority of electronic correlation effects across a large range of systems. For non-covalent interactions, QMC has been shown to describe interactions in dimers[3] and water clusters[4, 5] about as well as the best traditional quantum chemistry methods (e.g. coupled-cluster theory with singles, doubles, and perturbative triples CCSD(T)). For solids, benchmarking of the bulk modulus and equilibrium unit cell volume indicate that DMC is very competitive with state-of-the-art density functionals across a range of covalent, ionic, and van der Waals solids[6]. Various benchmarks against experiment on the G2 test set[7]

indicate that single-determinant DMC obtains a mean-absolute deviation of between 2.1[8] and 2.9 kcal/mole[9, 10] for atomization energies, which is on par with CCSD(T) when using a cc-pVQZ basis set.

With the introduction of robust optimization methods capable of simultaneously optimizing thousands of non-linear parameters, the prospect of being able to reduce the fixed-node error through massively parameterized and systematically improvable wavefunction ansatzs is becoming feasible. Though there are several promising classes of wavefunctions that might meet this criterion, for example antisymmetric geminal products [11], Pfaffians [12], linear-scaling generalized-valence-bond [13], multi-Slater determinant (MSD) wavefunctions [14, 15], often called "multideterminant wavefunctions", possess several advantages that make them quite attractive. First, they have been shown to be extremely accurate. Diffusion Monte Carlo (DMC) benchmarks over the G2 test set of various trial wavefunctions based on multideterminant expansions have finally produced sub-chemical accuracy for atomization energies, and near chemical accuracy for total energies [8, 10]. For first row atoms and dimers, MSD's are able to routinely recover at least 99% of correlation energies [10, 16, 17]. MSD's have also been shown to be able to accurately describe the dissociation of the C2 and N2 dimers [18].

MSD based QMC algorithms possess some nice properties in contrast to other wavefunction forms. First, there exist fast update formulae and compression algorithms for MSD's, which do not significantly affect the scaling of the QMC algorithm[19–21]. Second, optimization is fairly stable, since the expansion is built up from a linear combination of Slater determinants with variable coefficients. Third, much like in traditional QMC calculations where mean-field calculations help construct a starting ansatz for the Slater determinant, traditional quantum chemistry methods can be used to construct a reasonable starting guess for single-particle orbitals and important determinants. Lastly, once we have a procedure for constructing excited determinants, the number of included determinants becomes an adjustable parameter that will eventually converge to the correct result in the limit that we include all possible determinants. In practice, even the inclusion of tens to hundreds of determinants typically leads to significant improvements in the resulting trial wavefunctions.

Whereas in quantum chemistry, there are well studied and employed prescriptions for building accurate and compact multideterminant wavefunctions, similar studies have not been performed in QMC. At the single determinant level, the impact of single particle or-

bitals on the fixed-node energy has already been demonstrated across a range of atoms and dimers [22], and for bulk transition metal oxides [23]. We instead propose to go beyond the single Slater-Jastrow level in this paper, systematically investigating the impact that common orbital choices and methods of choosing determinants for multideterminant wavefunctions has on the fixed-node error in the equilibrium and stretched carbon dimer. Not only does this system possess a significant amount of static correlation (even in equilibrium), but there exist highly accurate full CI calculations describing ground and excited state energies from equilibrium all the way to the dissociation limit [24, 25]. After discussing the computational details, we will investigate how the fixed-node energy changes at the single-Slater and MSD level with respect to orbitals taken from methods like Hartree-Fock, DFT, and multi configuration self-consistent field methods (MCSCF). We will also investigate how quickly common methods of generating determinant expansions converge. With this information in hand, we then discuss which methods produce lowest and most rapidly converging energies within the QMC framework, analyze the relevant physics responsible for this behavior, and then discuss how these observations relate to extending MSD wavefunctions to solids.

II. COMPUTATIONAL DETAILS

In this section, we will describe the generation of single-particle orbitals and the schemes used in the generation and selection of determinants. Quantum chemistry calculations were performed with the GAMESS-US package [26, 27]. All results reported in this article, including both QMC and quantum chemistry calculations, used Burkatzki-Fillipi-Dolg (BFD) energy-consistent effective core potentials (ECP) to represent carbon along with the associated basis sets [28, 29]. Unless otherwise stated, we used the BFD basis set consistent with cc-pV5Z.

A. QMC

Our trial wavefunction ansatz will be of the multi-Slater determinant form, which is expressible as follows:

$$\Psi_T = e^{-J} \sum_{k=0}^{N_{CSF}} \alpha_k \Phi_k \quad (1)$$

Here J is a symmetric real-space Jastrow term. The set $\{\Phi_0, \dots, \Phi_{N_{CSF}}\}$ consists of N_{CSF} antisymmetric configuration state functions (CSF), and the set $\{\alpha_0, \dots, \alpha_{N_{CSF}}\}$ are linear coefficients. CSF's are spin and space adapted linear combinations of Slater determinants, and are used because they dramatically cut down on the number of degrees of freedom for our wavefunction parameterizations. They can be written as

$$\Phi_k = \sum_{i=0}^{N_k} c_i^k \det(M_i^\uparrow) \det(M_i^\downarrow) \quad (2)$$

Here, $M_i^{\uparrow(\downarrow)}$ is the Slater matrix for the up (down) electrons, whose elements are $[M_k^{\uparrow(\downarrow)}]_{ij} = \phi_j(r_i^{\uparrow(\downarrow)})$. The ϕ_j are single particle orbitals taken from the set $\{\phi_0, \dots, \phi_{N_{orb}}\}$, and $r_i^{\uparrow(\downarrow)}$ is the real-space 3D position of the i -th up (down) electron. N_{orb} denotes the total number of single-particle orbitals. The set of coefficients $\{c_i^k\}$ and the number of determinants N_k are fixed by symmetry.

For the symmetric Jastrow term J , we use a sum of spin-dependent two and three-body terms and a spin-independent one-body term. For the one and two body spin-dependent terms, we used a radially symmetric b-spline functional form with 10 knots and a cutoff radius of 10 bohr. For the three-body term, we used standard electron-electron-ion terms with radially symmetric functions expanded in third order polynomials. No electron-ion cusp condition needs to be applied to any of the Jastrow terms, since we are using BFD ECPs which are finite at the origin.

Once we have chosen the orbital set and built a set of CSF's, we use the linear method [30, 31] to minimize the VMC energy of Ψ_T with respect to all Jastrow parameters and the CSF coefficients. We performed 16 iterations of energy minimization, using 128,000 samples for the first 10, and 640,000 for the last 6. This typically leads to VMC energies converged to within 0.5 mHa.

Once we had a VMC optimized trial wavefunction, we performed an extended diffusion monte carlo simulation. We determined after performing a time-step extrapolation and population study that a time step of $\tau = 0.005Ha^{-1}$ and a walker population of 2560 was sufficient to ensure a systematic error of less than 0.2 mHa, which is comparable to the

statistical error in our simulations. We used single-particle moves and collected data over 250,000 sweeps.

All optimizations and QMC simulations were performed using the QMCPACK software package [32, 33]. MSD evaluations and updates were accomplished using the fast-update algorithm of Clark et. al. [19].

B. Choosing the CSF's

Given a set of single particle orbitals, the question becomes how we should choose the CSF's to use in our trial wavefunction. As the number of possible CSF's grows combinatorially with the size of our basis set, searching the full configuration interaction space (full CI) is prohibitively expensive. Instead, we will restrict our attention to various truncated CI spaces, which restricts the number of CSF's to a reference state and all those accessible by some maximum number of excitations into a set virtual orbital space. All following methods are standard in the quantum chemistry community, but we present them here only for clarity.

The single reference truncated CI methods we will use are CISD and CISDTQ. CISD stands for "configuration interaction with singles and doubles", meaning one starts from a single reference determinant and considers a determinantal subspace spanned by all determinants that differ from the reference by a single or double excitation into a set of N_v "virtual" orbitals. The CISDTQ method is similar, but in addition considers triple (T) and quadruple (Q) excitations into the set of virtual orbitals.

The main multi-reference CI method we will use is identical in spirit to CISD, but instead of considering single and double excitations out of a single determinant, we consider single and double excitations out of a multiconfigurational wavefunction. The multireference wavefunction is constructed by first taking a linear combination of all determinants in a "complete-active space", which is constructed by designating N_c orbitals as "core orbitals", N_a orbitals as "active", and then considering the set of all determinants which can be obtained by distributing N_e electrons among N_c doubly occupied core and N_a active orbitals. We will abbreviate the complete active space constructed in this manner "CAS(N_e, N_a)". The energy is then minimized with respect to the linear coefficients. The CSF's constructed by considering single and double excitations from a multireference wavefunction built from

CAS(N_e, N_a) is sometimes called “second order configuration interaction”, and we will abbreviate it as SOCI(N_e, N_a). All multireference wavefunctions in this paper use CAS(8,8).

As the number of CSF’s in such a space is still often too large for practical QMC calculations, our approach will be to first solve the problem with a particular form of truncated CI or multi-reference CI with a finite virtual space, which gives us $\Psi_{CI} = \sum_k \alpha'_k \Phi_k$. Using the CSF coefficients from this method, we include in our trial wavefunction all CSF’s where the magnitude of the coefficient is larger than some cutoff $|\alpha'_i| > \alpha_{cut}$. Notice that the weight of a particular CSF is completely dependent on the orbital set used in the expansion.

C. Orbitals

A major question we will explore in this work is how sensitive is the fixed-node energy of a multideterminant to the choice of single particle orbitals. Accordingly, we generated orbitals from several of the main types of mean field and many-body methods used in the quantum chemistry community. Before delving into the details of each, we note that all single-particle orbitals were calculated using the GAMESS-US quantum chemistry package.

At the mean field level, we self-consistently calculated orbitals at the Hartree-Fock and DFT levels of theory. Hartree-Fock orbitals will be abbreviated as “HF” orbitals in this paper. For the DFT calculations, we considered orbitals generated from two different choices of functionals: the semi-local gradient corrected functional, PBE [34], and the hybrid exchange functional B3LYP[35]. These functionals were chosen because they represent popular choices and classes of functionals used in the community. We will reference these as “PBE” and “B3LYP” orbitals in this paper. All mean-field calculations were restricted closed-shell calculations.

Going beyond the mean-field level, the most powerful many-body methods we use fall under the umbrella of so-called multiconfigurational self-consistent field methods (MCSCF). These methods produce an optimal set of orbitals consistent with a multiconfigurational wavefunction ansatz, in contrast to Hartree-Fock which yields optimal orbitals for a single determinant wavefunction. The first method we consider is complete active space self-consistent field (CASSCF) [36], which first assumes a wavefunction constructed from linear combination of all determinants in a CAS(N_e, N_a), and then self consistently optimizes both the orbital and CSF coefficients. Note that only orbitals in the active space are optimized.

We define the orbitals calculated from this method as “CASSCF(N_e, N_a)”.

The other multiconfigurational method we will use is called “self-consistent second-order CI” [37]. This method employs the same wavefunction ansatz as SOCI(N_e, N_a) described in the previous section, but additionally optimizes the single particle orbitals used to construct the CSF’s. We will refer to orbitals taken from this method as “SOCI(N_e, N_a)”, taking care to distinguish it from the “SOCI(N_e, N_a)” CSF’s when such ambiguity is likely.

The last many-body method we consider involves constructing natural orbitals from second order Møller-Plesset perturbation theory (MP2) [38]. Starting from Hartree-Fock orbitals, natural orbitals were obtained by diagonalizing the one-body density matrix calculated with MP2. We denote these orbitals as “MP2NO” in the paper.

D. Extrapolations

The previous method gives us a way of selecting a subset of our chosen truncated CI space deemed important by quantum chemistry. We are also concerned with what the fixed-node energy would be in the limit that we included all determinants in some given truncated CI space (not the full CI space). Since we are using quantum chemistry methods to screen determinants, Umrigar *et. al* [30, 31] pointed out that we can extrapolate the fixed node energy with respect to the sum of squares for the quantum chemistry CSF coefficients corresponding to the CSF’s included in the trial wavefunction. Formally, this is written as $|\mathcal{N}|^2 = \sum_k^{N_{CSF}} |\alpha'_k|^2$, and has the nice property that $|\mathcal{N}|^2 \rightarrow 1$ as we include all determinants in the determinantal subspace, i.e. when N_{CSF} equals the number of CSF’s in the complete truncated CI space. Consistent with previous work[30, 31], this leads to reliable extrapolation of both VMC and DMC energies and we will rely on such extrapolations to obtain converged results in this paper.

E. Reference Energies

Exact energies were estimated using a combination of explicitly correlated coupled cluster theory with singles, doubles, and perturbative triples (CCSD(T)-R12), and full configuration interaction quantum Monte Carlo (FCIQMC) [39–41]. The FCIQMC method performs a stochastic full configuration interaction calculation and has been shown to be extremely

accurate [39–41]. While it is currently limited to small systems, it provides very accurate results (typically within 0.1 mHa of exact results) for system sizes too large for traditional full CI approaches. A recent article by Booth *et. al.* [42] makes a detailed analysis of the dissociation curve of the carbon dimer showing essentially exact results for various atomic basis sets, an estimate of the complete basis set limit (CBS) is also provided. Table II E shows the energy difference between their FCIQMC results and CCSD(T)-R12 calculations as a function of basis set. While the convergence of the total energy is slow with basis set and requires basis set extrapolation techniques for converged results, the convergence of energy differences between these two methods converges quickly with basis set. As a result, we estimate the exact energies at the two studied dimer configurations from a combination of extrapolated CCSD(T)-R12 energies and differences between FCIQMC and CCSD(T)-R12 at an appropriate finite basis set. In other words we define: $E_{exact} = E_{CCSD(T)-CBS} + \Delta E^{TZ}$, where $\Delta E^{TZ} = E_{FCIQMC}^{TZ} - E_{CCSD(T)}^{TZ}$. We were unable to use the results of Booth, *et. al.* [42] directly because they do not use BFD ECPs in the calculations and they only provide results for the $X^1\Sigma_g^+$ state. As we see below, the ground state of the stretched configuration is $B^1\Delta_g$. As a result, we performed our own FCIQMC [47] calculations with same BFD ECP used elsewhere in this study using a code developed by one of the authors. We also provide FCIQMC results without using BFD ECPs to compare against the results reported by Booth, *et. al.*

III. CARBON DIMER

The carbon dimer is a well known difficult test case for *ab initio* quantum chemistry methods. Even in its equilibrium geometry, the ground-state of the carbon dimer possesses some multi-reference character [24, 25]. After stretching the dimer beyond 1.6 Å, the combination of a level crossing and near degeneracies between the ground state and low lying excited states (see Figure 1) causes a break down of single-reference methods. For these reasons, the carbon dimer is a reasonable simple system to use for identifying any pathologies or sensitivities in MSD based QMC calculations.

For both the equilibrium geometry (R=1.2424 Å) and a particular stretched geometry (R=1.8 Å), we will investigate three major properties related to the choice of orbitals and determinants used in our MSD expansion. First, we will investigate the influence of orbital

	cc-pVDZ	cc-pVTZ	cc-pVQZ
Equilibrium: no ECP $X^1\Sigma_g^+$			
Booth, <i>et al.</i>	-	-1.86(2)	-1.70(8)
this study	-1.85(1)	-1.84(2)	-
Equilibrium: BFD-ECP $X^1\Sigma_g^+$			
this study	-1.79(2)	-1.78(2)	-
Stretched: BFD-ECP $B^1\Delta_g$			
this study	-6.7(1)	-6.9(1)	-

TABLE I: Energy difference (in mHa) between FCIQMC and CCSD(T)-R12 calculations for the carbon dimer at the two configurations used in this study. The dimer at the equilibrium configuration ($R=1.24253 \text{ \AA}$) has an electronic ground state state of symmetry $X^1\Sigma_g^+$, while the stretched configuration ($R = 1.8 \text{ \AA}$) has a ground state with symmetry $B^1\Delta_g$. We also include the FCIQMC results of Booth *et al.* from Ref. [42] for comparison with our results.

sets on the single determinant DMC energies. This will help us understand any fundamental difference (or lack of) on the nodal structure of the reference determinant in each orbital set. Then, we will look at how the choice of orbitals used in the multi-Slater determinant construction affects the ultimate accuracy of the DMC calculations. In this case, since we are only interested on the influence of the orbital set, we use the best configuration selection scheme to construct the trial wave function. Finally, we study the combined influence of orbital set and configuration selection on the ultimate accuracy of DMC energies.

A. Equilibrium Configuration

To begin the discussion of the equilibrium carbon dimer, we look at the fixed-node energies of various single Slater-Jastrow type wavefunctions, presented in Table III A. These DMC calculations differ only on the choice of single-particle orbitals used in the determinant. We find that Hartree-Fock orbitals recover the smallest amount of correlation energy at about 87.2%. We gain about 1% of the correlation energy by instead using MP2 natural orbitals with 88.3%, and then another 0.4-0.5% with PBE, BLYP, CASSCF, or SOCI orbitals, these last four being statistically indistinguishable from one another. Though we can conclude

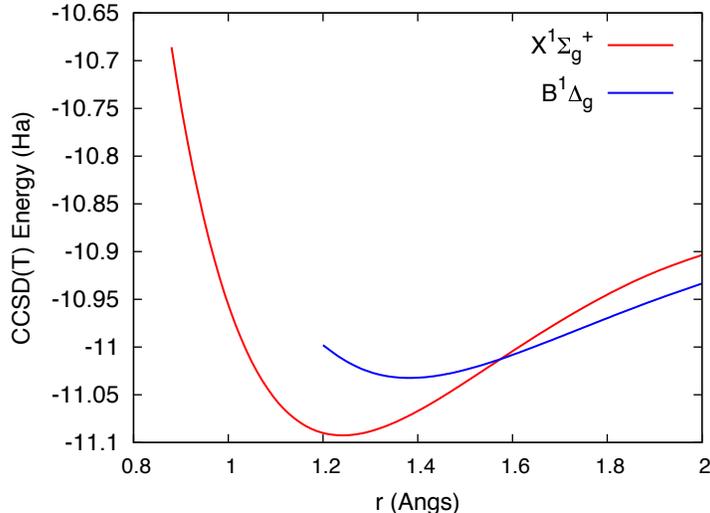


FIG. 1: (Color Online) CCSD(T)-R12 energy of the $X^1\Sigma_g^+$ and $B^1\Delta_g$ states as a function of atomic distance, using the BFD ECP and a cc-pVQZ atomic basis set. Note the level crossing around $R \sim 1.6$ Å.

from this that DFT and higher order quantum chemistry methods yield lower energies and thus better nodes than Hartree-Fock or MP2, we see that at the single Slater-Jastrow level, DMC is relatively insensitive to the choice of basis set, having a spread of only 1.7% of the correlation energy for all orbitals considered. Not only this, but we are still missing approximately 11% of the correlation energy of the C2 dimer.

Now we consider the impact that orbital choice has on the quality of multi-Slater determinant wavefunctions. To simplify the discussion, we choose to generate all multideterminant wavefunctions in this test using the SOCI(8,8) method described in Section II B. Because this method is fundamentally multireference, it should be more effective at identifying important configurations than CISD or even CISDTQ, hopefully allowing us to disentangle the effects of orbital choice from CSF choice as much as possible.

For all the orbitals tested at the single Slater determinant level, we show in Figure 2 the dependence of the fixed node energy on both the CI wavefunction norm (as described in section II D), and the number of CSF's used in our MSD wavefunction. The different colors denote the different choice of orbitals, and the black line denotes the reference taken from a CCSD(T)-R12 calculation extrapolated to the complete basis set limit. Not surprisingly, the inclusion of only a few CSF's dramatically lowers the fixed-node energy, allowing us to

Method	Total Energy (Ha)	% CE
SD-DMC-HF	-11.0494(4)	87.2
SD-DMC-CASSCF	11.0561(3)	88.8
SD-DMC-MP2NO	-11.0541(4)	88.3
SD-DMC-PBE	-11.0565(2)	88.9
SD-DMC-B3LYP	-11.0556(3)	88.7
SD-DMC-SOCI	-11.0556(7)	88.7
CCSD(T)-CBS	-11.10067	99.6
Estimate-Exact	-11.10244(2)	100.0

TABLE II: Energy of the carbon dimer at the equilibrium bond length from single determinant DMC calculations using orbitals generated from a selection of methods. The method abbreviations are described in the text. CCSD(T)-CBS refers to CCSD(T)-R12 calculations obtained from a 3-point extrapolation to the complete basis set limit using cc-pV[T,Q,5]Z basis sets. Estimated-exact results are also included, which were obtained from corrections to CCSD(T) calculations obtained from the FCIQMC method [42]. The percentage of the correlation energy recovered by each method is also presented.

recover an additional 7.5% of the correlation energy beyond the single Slater-Jastrow level. Extrapolating on the norm of the truncated wave function (to the limit of a full SOCI(8,8) wavefunction) we find that all orbitals sets result in DMC energies within 4 mHa of the exact answer. As expected, the best choice is the SOCI(8,8) orbitals, which are about 2mHa away from the exact result, and the worst being MP2, which is 4mHa higher. Overall this example seems to indicate that as long as we perform an aggressive search of important configurations in the full CI space, the extrapolated energies will be reasonably insensitive to the choice of basis set.

A final point that must be discussed is the convergence of the DMC energy as a function of the number of CSFs included in the calculation. While all orbital sets lead to similar extrapolated energies, the rate of convergence can be quite different. In this example, the use of nearly optimal SOCI(8,8) orbitals leads to energies within 4 mHa of the exact answer with just ~ 350 CSFs, while HF orbitals required over 2000-3000 CSFs for a similar accuracy.

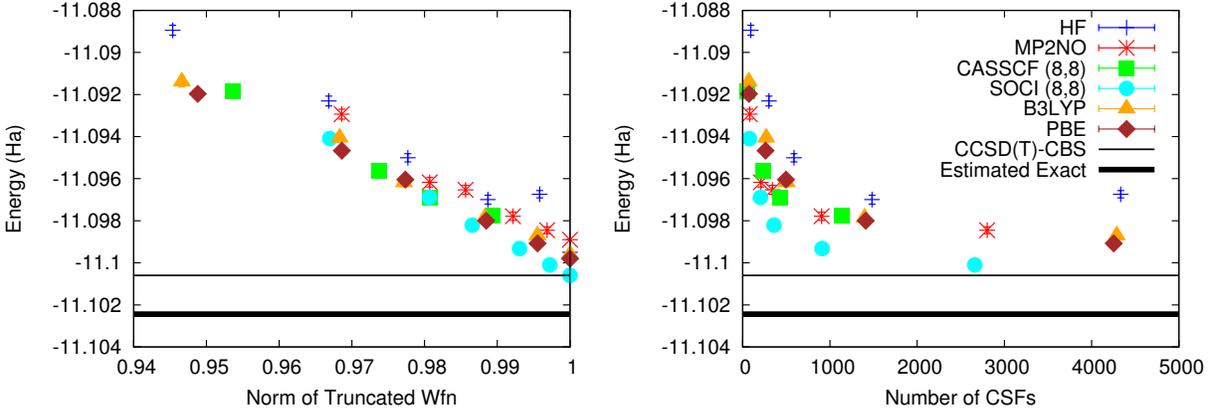


FIG. 2: (Color online) DMC energy of the carbon dimer in the equilibrium configuration as a function of the norm of the truncated trial wave function (left) and as a function of the number of CSFs (right). Results are shown for all the molecular orbital sets considered in this work. CCSD(T)-CBS and estimated exact results are also shown for comparison. Error bars are smaller than the markers.

This, of course, merely shows the fact that SOCI(8,8) orbitals have been optimized for a compact CI representation through the SCF approach. Nonetheless, this provides clear justification for the search of optimized orbital sets directly within a QMC framework.

Having looked at how the convergence of the fixed-node energy depends on choice of orbitals, we lastly consider how the convergence depends on the method used to generate configurations. We consider selecting configurations from CISD, CISDTQ, and SOCI(8,8), using virtual orbital spaces of both 20 and 50 orbitals for all methods. Figure 3 shows the convergence of the fixed-node energy with respect to number of CSF's (top) and norm of the MSD wavefunction (bottom) using HF orbitals (first column), B3LYP orbitals (second column), and SOCI orbitals (last column). The different colors represent the different quantum chemistry methods for choosing the excited determinants. Table III A contains the fixed-node energies extrapolated to unit norm from the data given in Figure 3. The remaining orbital sets are not shown in the figure. We find that when using HF or B3LYP orbitals, there is a large degree of sensitivity in the fixed-node energy to both the quantum chemistry method and the size of the virtual orbital space used to construct the excited determinants. CISD using 20 valence orbitals is the worst, missing about 3.6 and 2.8% of the correlation energy for HF and B3LYP orbitals respectively. Including triple and quadruple excitations

or using SOCI with 20 virtual orbitals (CISDTQ-20 and SOCI-20 in the plot), or enlargening the space of double excitations to 50 virtual orbitals (CISD-50), gives a noticeable improvement in energy. This amounts to a recovery of between 1.4% and 1.7% for HF orbitals, and between 1.0% and 1.3% for B3LYP orbitals in the correlation energy. Lastly, CISDTQ and SOCI with 50 virtual orbitals give the best results (and largely indistinguishable results), missing approximately 0.6% and 0.8% of the correlation energy for both the HF and B3LYP orbitals.

Looking now at the results obtained using SOCI orbitals, we see a qualitatively different picture. Here, we can separate the convergence behaviors into two classes: those containing just single and double excitations (e.g. CISD), and those that consider higher-order excitations (CISDTQ and SOCI). CISD configurations converge to approximately 98.4% regardless of the size of the virtual orbital space, and does so rapidly but nonlinearly in the limit that we include all determinants. All other methods that include higher order excitations—CISDTQ explicitly and SOCI implicitly—converge to approximately 99.5% of the correlation energy— independent of the size of the virtual orbital space. We note that all these methods converge nearly linearly to this result and all with approximately the same slope, in contrast to the CISD set of determinants.

B. Stretched Configuration

In this section, we will repeat the analysis we did for the equilibrium dimer, however focusing more on the qualitative/quantitative differences emerging in the stretched case. In this case there is a stronger multi-reference character in the ground state wavefunction. If we attempt to describe this system perturbatively from a single reference configuration, we should expect to see much more sensitivity to the starting wavefunction ansatz and number/type of included excitations than in the equilibrium dimer.

Table III B shows a summary of the DMC energies obtained using single determinant wavefunctions with HF, B3LYP and SOCI orbital sets. At the single determinant level, we find no significant qualitative or quantitative change from the equilibrium configuration in the dependence of the fixed-node energy on the choice of single particle orbitals. As in the equilibrium case, we can recover about 88.4% of the correlation energy by using SOCI or B3LYP orbitals. Hartree-Fock is again worse than these two choices of orbitals, but only by

Method	CISD	CISDTQ	SOCI
HF-20	-11.0876(2) [96.4]	-11.0924(3) [97.6]	-11.0944(3) [98.1]
HF-50	-11.0933(2) [97.8]	-11.0996(3) [99.3]	-11.0998(1) [99.4]
CASSCF-20	-11.0911(2) [97.3]	-11.0945(2) [98.1]	-11.0959(2) [98.4]
CASSCF-50	-11.0944(2) [98.1]	-11.0995(3) [99.3]	-11.0993(1) [99.3]
MP2NO-20	-11.0945(1) [98.1]	-11.0980(2) [98.9]	-11.0982(3) [99.0]
MP2NO-50	-11.0952(2) [98.3]	-11.0990(3) [99.2]	-11.0989(1) [99.2]
PBE-20	-11.0911(2) [97.3]	-11.0953(2) [98.3]	-11.0964(3) [98.6]
PBE-50	-11.0946(1) [98.1]	-11.0996(3) [99.3]	-11.0998(2) [99.4]
B3LYP-20	-11.0908(2) [97.2]	-11.0952(2) [98.3]	-11.0961(3) [98.5]
B3LYP-50	-11.0948(2) [98.2]	-11.0992(3) [99.2]	-11.0997(2) [99.4]
SOCI-20	-11.0957(1) [98.4]	-11.1002(2) [99.5]	-11.1006(3) [99.6]
SOCI-50	-11.0962(2) [98.5]	-11.1005(2) [99.5]	-11.1006(1) [99.6]

TABLE III: Extrapolated energies of the carbon dimer at the equilibrium bond length from multi-determinant DMC calculations using orbitals generated from a selection of methods. All quantities reported correspond to extrapolations of the DMC energies with the norm of the truncated wavefunction included in the MSD expansion. Refer to the text for a description of the abbreviations. The percentage of the correlation energy recovered by each method is also presented.

about 1% of the correlation energy.

We now look at the impact of orbital choice on a MSD expansion based on SOCI(8,8) with 50 virtual orbitals. The results are shown in Figure 4. Despite the fact that this is a more complicated problem, all considered orbital sets recover around 99% of the correlation energy. Specifically, B3LYP and SOCI orbitals recover almost the same amount of correlation energy as in the equilibrium case (between 99.3% and 99.6%). Even HF orbitals recover 98.8% of the correlation energy (though less than the 99.4% in equilibrium). Looking at the rate of convergence of the fixed-node energy to the full SOCI(8,8) set of determinants, we find that once again that the SOCI(8,8) orbitals are more rapidly convergent, followed by B3LYP and HF. Notice how in this case only several hundred determinants are needed to obtain results that are better than CCSD(T). This is an indicator of the stronger multi-reference character

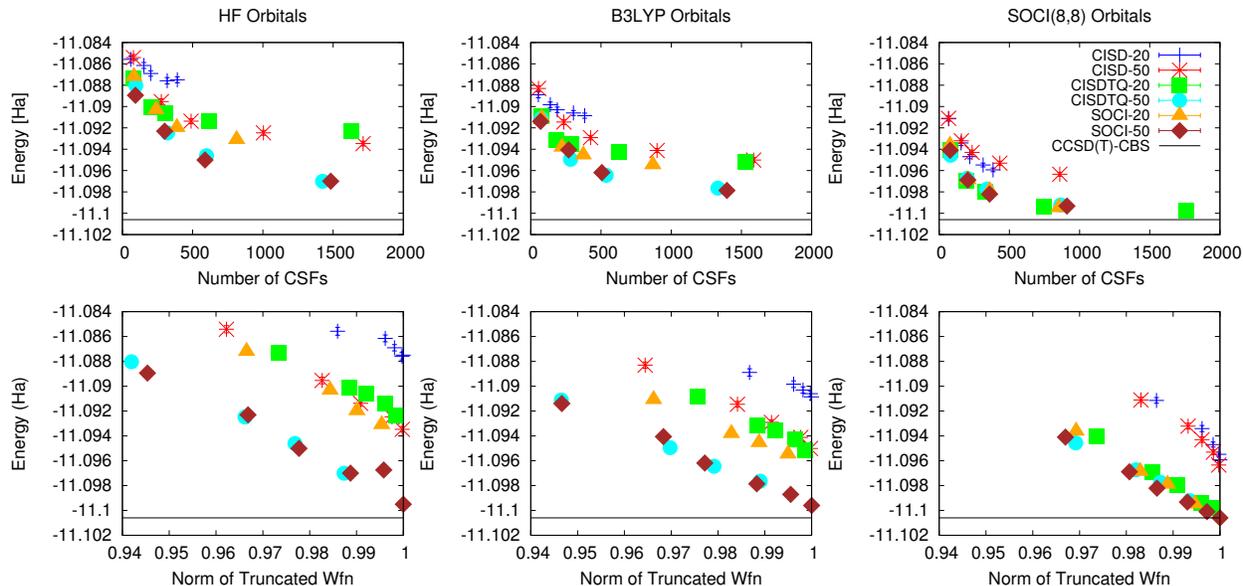


FIG. 3: (Color online) DMC energy of the carbon dimer at equilibrium as a function of the number of CSF's (top) and norm of the MSD wavefunction (bottom) using HF orbitals (first column), B3LYP orbitals (second column), and SOCI orbitals (last column). The different colors represent the different quantum chemistry methods used for choosing the excited determinants. The CCSD(T)-CBS energy is shown for comparison. Error bars are smaller than the markers.

of the electronic state.

Figure 5 shows the convergence of the fixed-node energy with respect to both the number of CSF's (top row) and the norm of the CI wavefunction (bottom row) for HF orbitals (first column), B3LYP orbitals (second column), and SOCI orbitals (last column). Table III B shows a summary of the extrapolated DMC energies. As expected, selecting configurations using SOCI leads to noticeably lower energies in all orbital sets. They also lead to similar rates of convergence with respect to the number of CSF's included in the wavefunction and to similar extrapolated energies. On the other hand, there is a strong variation on the amount of correlation energy recovered when less aggressive configuration selection algorithms are chosen. This is very pronounced when HF and B3LYP orbital sets are used.

IV. DISCUSSION

Several important observations can be made from the two examples presented above.

Method	Total Energy (Ha)	% CE
SD-DMC-HF	-10.9407(2)	87.5
SD-DMC-B3LYP	-10.9440(2)	88.5
SD-DMC-SOCI	-10.9439(2)	88.4
CCSD(T)-CBS	-10.97725	98.0
Estimated-Exact	-10.9841	100.0

TABLE IV: Summary of energies of the carbon dimer at a stretched configuration from DMC calculations using orbitals generated from a selection of methods. Refer to the text for a description of the abbreviations. The percentage of the correlation energy recovered by each method is also presented.

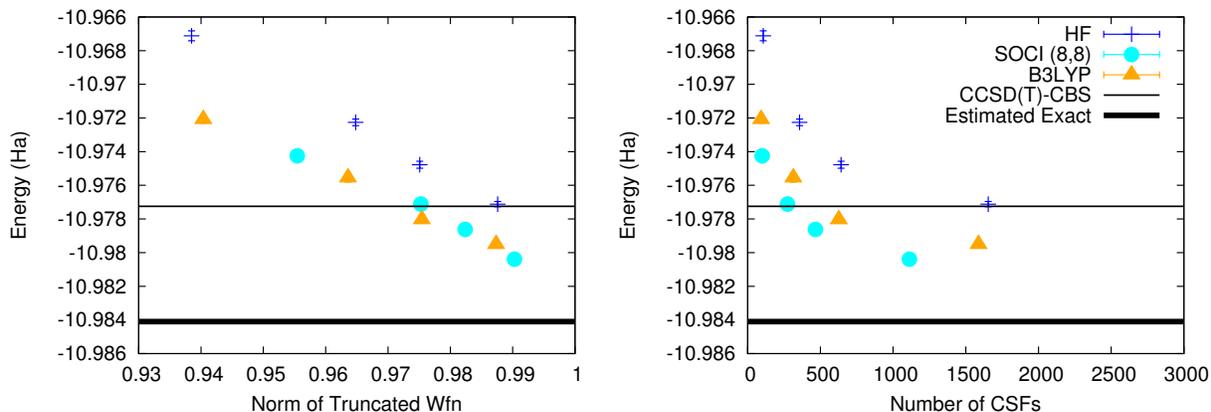


FIG. 4: (Color online) DMC energy of the carbon dimer in the stretched configuration as a function of the norm of the truncated trial wave function (left) and as a function of the number of CSFs (right). Results are shown for HF, B3LYP and SOCI orbital sets. CCSD(T)-CBS and estimated exact results are also when for comparison. Error bars are smaller than the markers.

First, the inclusion of several hundred configurations leads to large improvements in the percentage of correlation energy recovered relative to single Slater Jastrow wavefunctions. This allows us to recover at least 95% of the correlation for both the equilibrium and stretched geometries for all methods we considered, in contrast to the 89% recovered correlation energy we saw with single determinant wavefunctions. In trying to recover the remaining 5% however, we observed that the fixed-node energy from the MSD wavefunction was sensitive to both the choice of orbitals and method used to generate the CSF's. Both

Method	CISD	CISDTQ	SOCI
HF-20	-10.9680(2) [95.4]	-10.9719(4) [96.5]	-10.9738(4) [97.0]
HF-50	-10.9740(2) [97.1]	-	-10.9799(3) [98.8]
B3LYP-20	-10.9708(2) [96.2]	-10.9756(2) [97.6]	-10.9769(3) [97.9]
B3LYP-50	-10.9748(1) [97.3]	-10.9816(4) [99.3]	-10.9818(4) [99.3]
SOCI-20	-10.9747(2) [97.3]	-10.9803(3) [98.9]	-10.9819(3) [99.4]
SOCI-50	-10.9755(2) [97.5]	-10.9813(3) [99.2]	-10.9824(3) [99.5]

TABLE V: Summary of energies of the carbon dimer at the stretched configuration from DMC calculations using orbitals generated from several different methods. Refer to the text and the caption of figure III A for a description of the abbreviations. The percentage of the correlation energy recovered by each method is also presented.

examples led to qualitatively similar results: SOCI orbitals produced the lowest energies, followed by B3LYP, with HF orbitals producing the worst energies. This is expected given the level of sophistication of each method and the level at which each method treats correlation. The speed of convergence of the energy with the number of configurations included in the MSD expansion also varied significantly depending on the orbital set and the configuration selection algorithm. On the other hand, regardless of the quality of the orbitals used, the extrapolated DMC energies were very similar and quite accurate when an aggressive configuration selection scheme (SOCI) was used. The existence of stronger multi-reference character in the stretched configuration did not lead to any significant differences in the overall dependence of the energy with orbital set and configuration selection. Even at the single determinant level both configurations resulted in quantitatively similar results.

Second, we observed another obvious benefit of using “good” orbitals in QMC calculations other than obtaining lower energies. We observed that convergence of the fixed-node energy to the full truncated CI space limit was far more smooth and linear in the case of good orbitals than with poor orbitals. This is of extreme importance, because not only can we get away with using fewer CSF’s to achieve a given fixed-node error in a QMC calculation, but we can save a lot of computer time by being able to meaningfully extrapolate to large determinant set limits with just a few CSF’s.

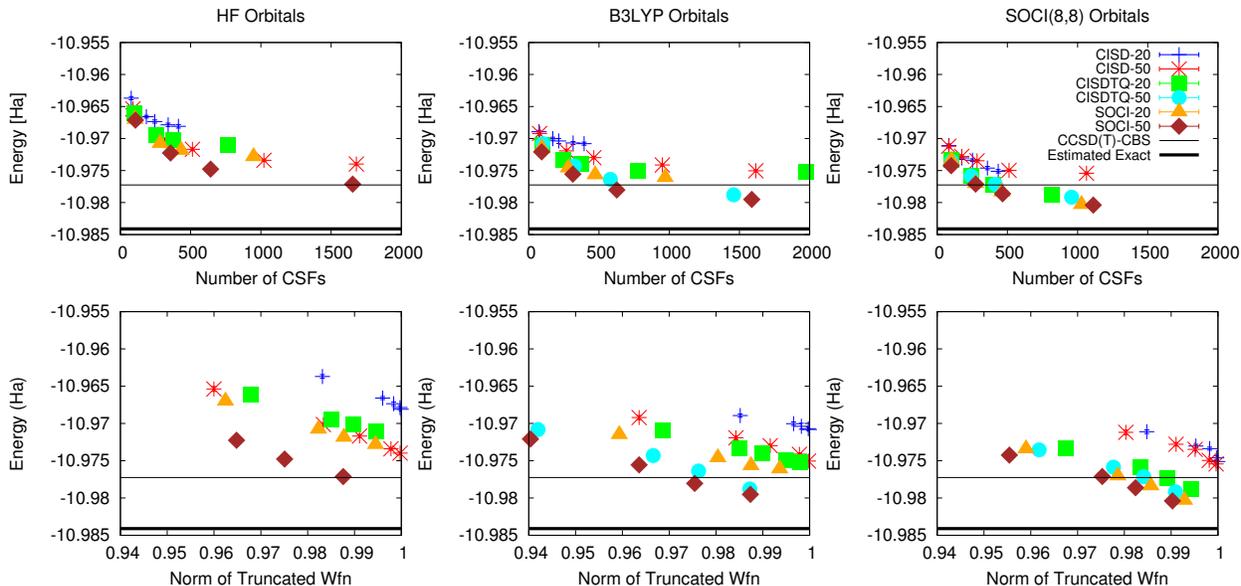


FIG. 5: (Color online) DMC energy of the carbon dimer at the stretched configuration as a function of the number of CSF's (top) and the norm of the MSD wavefunction (bottom) using HF orbitals (first column), B3LYP orbitals (second column), and SOCI orbitals (last column). The different colors represent the different quantum chemistry methods used for choosing the excited determinants. The CCSD(T)-CBS and estimated exact energies are shown for comparison. Error bars are smaller than the markers.

From this analysis it is clear that both orbital optimization and configuration selection are important aspects in the construction of accurate MSD wavefunctions in QMC. While we can rely on high level quantum chemistry methods for both tasks in small molecular systems, this is clearly not possible for larger molecules and bulk systems. In this case, we must rely on alternative methods to perform these tasks, ideally using methods based entirely on QMC. There are two simple alternatives for orbital set generation. The simplest approach is to perform an optimization of the orbital set at the VMC level using a multideterminant trial wave function. This is typically restricted to MSD expansions over small active space [18, 30, 31], since the choice of configurations is frozen throughout the process. The second approach involves the use of natural orbitals obtained from QMC calculations. While the calculation of natural orbitals requires the calculation of the one-particle reduced density matrix, which can be computationally expensive, the resulting orbitals can be very accurate and the calculation can be performed self-consistently with increasingly more complicated

trial wave-functions at each step. We are currently investigating both alternatives. The results will be presented in a future publication.

The selection of determinant configurations using QMC, given some orbital set, has received considerably less attention in the community so far. In principle, it is straightforward to use VMC optimization to select important configurations. The main disadvantage is the need to perform an optimization process including all possible configurations simultaneously, which given the negligibly small number of important configurations in an otherwise exponentially large configuration space leads to both inefficiency and a low chance of success in practice. Algorithms that perform this task perturbatively, without the need to explicitly optimize all the configurations simultaneously, have recently shown quite a deal of promise [43]. The recently introduced self-healing algorithm [44, 45] offers another alternative for both the configuration selection and the optimization of the resulting linear parameters at the DMC level. Unfortunately, the method suffers from the same problem as a direct VMC optimization of needing to explicitly treat all possible configurations directly in the DMC calculation. Nonetheless, the method offers important insight into the optimization of wave-functions at the DMC level, which we believe will be influential in the development of new configuration selection algorithms in the future.

V. CONCLUSIONS

In this paper, we have analyzed the effects that various combinations of orbital set choice, configuration selection method, and number of included configurations have on the fixed-node energy. Specifically, we found that convergence of the trial wavefunction with respect to added configurations can be dramatically improved through the joint choices of orbital sets that take into account electronic correlation and through select inclusion of highly excited determinants through methods like SOCI.

Given the gains we see at this level, we believe it is necessary to be able to jointly optimize orbital sets and intelligently choose configurations without the aid of high-level quantum chemistry calculations, especially since much larger molecules and solids are currently beyond the scope of most quantum chemistry methods. We believe that reasonable modifications of currently extant methods like VMC optimization with many parameters and perturbative configuration selection or self-healing, as well as self-consistent hybrid

approaches described in our previous discussion, are the most promising avenues towards accomplishing this goal. Eventually, it is hoped that algorithmic advancements will render large scale multideterminant calculations as robust and far more accurate than a routine Slater-Jastrow QMC calculation.

-
- [1] W. M. C. Foulkes, L. Mitas, R. J. Needs, and G. Rajagopal, *Reviews of Modern Physics* **73**, 33 (2001), ISSN 0031-9007.
 - [2] M. Morales, R. Clay, C. Pierleoni, and D. Ceperley, *Entropy* **16**, 287 (2013), ISSN 1099-4300, URL <http://www.mdpi.com/1099-4300/16/1/287/>.
 - [3] M. Dubecký, P. Jurečka, R. Derian, P. Hobza, M. Otyepka, and L. Mitas, *Journal of Chemical Theory and Computation* **9**, 4287 (2013), ISSN 1549-9618, URL <http://pubs.acs.org/doi/abs/10.1021/ct4006739>.
 - [4] B. Santra, A. Michaelides, and M. Scheffler, *The Journal of chemical physics* **127**, 184104 (2007), ISSN 0021-9606, URL <http://www.ncbi.nlm.nih.gov/pubmed/18020627>.
 - [5] B. Santra, A. Michaelides, M. Fuchs, A. Tkatchenko, C. Filippi, and M. Scheffler, *The Journal of chemical physics* **129**, 194111 (2008), ISSN 1089-7690, URL <http://www.ncbi.nlm.nih.gov/pubmed/19026049>.
 - [6] L. Shulenburger and T. Mattsson, *Physical Review B* **88**, 245117 (2013), ISSN 1098-0121, URL <http://link.aps.org/doi/10.1103/PhysRevB.88.245117>.
 - [7] L. A. Curtiss, K. Raghavachari, P. C. Redfern, and J. a. Pople, *The Journal of Chemical Physics* **106**, 1063 (1997), ISSN 00219606, URL <http://link.aip.org/link/JCPSA6/v106/i3/p1063/s1/&Agg=doi>.
 - [8] F. R. Petruzielo, J. Toulouse, and C. J. Umrigar, *The Journal of chemical physics* **136**, 124116 (2012), ISSN 1089-7690, URL <http://www.ncbi.nlm.nih.gov/pubmed/22462844>.
 - [9] J. C. Grossman, E. Schwegler, E. W. Draeger, F. Gygi, and G. Galli, *The Journal of chemical physics* **120**, 300 (2004), ISSN 0021-9606, URL <http://www.ncbi.nlm.nih.gov/pubmed/15267290>.
 - [10] M. A. Morales, J. McMinis, B. K. Clark, J. Kim, and G. E. Scuseria, *Journal of Chemical Theory and Computation* **8**, 2181 (2012), ISSN 1549-9618, URL <http://pubs.acs.org/doi/abs/10.1021/ct3003404>.

- [11] M. Casula, C. Attaccalite, and S. Sorella, *The Journal of chemical physics* **121**, 7110 (2004), ISSN 0021-9606, URL <http://www.ncbi.nlm.nih.gov/pubmed/15473777>.
- [12] M. Bajdich, L. Mitas, G. Drobný, L. Wagner, and K. Schmidt, *Physical Review Letters* **96**, 130201 (2006), ISSN 0031-9007, URL <http://link.aps.org/doi/10.1103/PhysRevLett.96.130201>.
- [13] F. Fracchia, C. Filippi, and C. Amovilli, *Journal of Chemical Theory and Computation* **8**, 1943 (2012), ISSN 1549-9618, URL <http://pubs.acs.org/doi/abs/10.1021/ct3001206>.
- [14] C. J. Umrigar, K. G. Wilson, and J. W. Wilkins, *Phys. Rev. Lett.* **60**, 1719 (1988), URL <http://link.aps.org/doi/10.1103/PhysRevLett.60.1719>.
- [15] Z. Sun, R. N. Barnett, and W. A. Lester Jr, *The Journal of chemical physics* **96**, 2422 (1992).
- [16] P. Seth, P. L. Ríos, and R. J. Needs, *The Journal of chemical physics* **134**, 084105 (2011), ISSN 1089-7690, URL <http://www.ncbi.nlm.nih.gov/pubmed/21361525>.
- [17] M. D. Brown, J. R. Trail, P. L. Ríos, and R. J. Needs, *The Journal of chemical physics* **126**, 224110 (2007), ISSN 0021-9606, URL <http://www.ncbi.nlm.nih.gov/pubmed/17581047>.
- [18] J. Toulouse and C. J. Umrigar, *The Journal of chemical physics* **128**, 174101 (2008), ISSN 0021-9606, URL <http://www.ncbi.nlm.nih.gov/pubmed/18465904>.
- [19] B. K. Clark, M. A. Morales, J. B. McMinis, J. Kim, and G. E. Scuseria, *The Journal of chemical physics* **135**, 244105 (2011), ISSN 1089-7690, URL <http://www.ncbi.nlm.nih.gov/pubmed/22225142>.
- [20] G. L. Weerasinghe, P. L. Ríos, and R. J. Needs, *Physical Review E* **89**, 023304 (2014), ISSN 1539-3755, URL <http://link.aps.org/doi/10.1103/PhysRevE.89.023304>.
- [21] P. K. V. V. Nukala and P. R. C. Kent, *The Journal of chemical physics* **130**, 204105 (2009), ISSN 1089-7690, URL <http://www.ncbi.nlm.nih.gov/pubmed/19485435>.
- [22] M. C. Per, K. a. Walker, and S. P. Russo, *Journal of Chemical Theory and Computation* **8**, 2255 (2012), ISSN 15499618.
- [23] J. Kolorenč, S. Hu, and L. Mitas, *Physical Review B - Condensed Matter and Materials Physics* **82**, 1 (2010), ISSN 10980121, 1003.2507.
- [24] M. L. Abrams and C. D. Sherrill, *The Journal of chemical physics* **121**, 9211 (2004), ISSN 0021-9606, URL <http://www.ncbi.nlm.nih.gov/pubmed/15538841>.
- [25] P. Su, J. Wu, J. Gu, W. Wu, and S. Shaik, pp. 121–130 (2011).
- [26] M. S. Gordon and M. W. Schmidt, in *Theory and Applications of Computational Chemistry:*

- The First Forty Years*, edited by C. E. Dykstra, G. Frenking, K. S. Kim, and G. E. Scuseria (Elsevier, Amsterdam, 2005), chap. 41, pp. 1167–1189, ISBN 978-0-444-51719-7.
- [27] M. W. Schmidt, K. K. Baldrige, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, et al., *Journal of Computational Chemistry* **14**, 1347 (1993), ISSN 0192-8651, URL <http://doi.wiley.com/10.1002/jcc.540141112>.
- [28] M. Burkatzki, C. Filippi, and M. Dolg, *The Journal of chemical physics* **129**, 164115 (2008), ISSN 1089-7690, URL <http://www.ncbi.nlm.nih.gov/pubmed/19045255>.
- [29] M. Burkatzki, C. Filippi, and M. Dolg, *The Journal of chemical physics* **126**, 234105 (2007), ISSN 0021-9606, URL <http://www.ncbi.nlm.nih.gov/pubmed/17600402>.
- [30] J. Toulouse and C. J. Umrigar, *The Journal of chemical physics* **126**, 084102 (2007), ISSN 0021-9606, URL <http://www.ncbi.nlm.nih.gov/pubmed/17343435>.
- [31] C. J. Umrigar, J. Toulouse, C. Filippi, S. Sorella, and R. G. Hennig, *Physical Review Letters* **98**, 110201 (2007), ISSN 0031-9007, URL <http://link.aps.org/doi/10.1103/PhysRevLett.98.110201>.
- [32] K. Esler, J. Kim, D. Ceperley, and L. Shulenburger, *Computing in Science & Engineering* **14**, 40 (2012), ISSN 1521-9615, URL <http://ieeexplore.ieee.org/lpdocs/epic03/wrapper.htm?arnumber=5601669>.
- [33] J. Kim, K. P. Esler, J. McMinis, M. A. Morales, B. K. Clark, L. Shulenburger, and D. M. Ceperley, *Journal of Physics: Conference Series* **402**, 012008 (2012), ISSN 1742-6588, URL <http://stacks.iop.org/1742-6596/402/i=1/a=012008?key=crossref.4ed57529bb119840d5ff59db8de48216>.
- [34] J. Perdew, K. Burke, and M. Ernzerhof, *Physical review letters* **77**, 3865 (1996), ISSN 1079-7114, URL <http://www.ncbi.nlm.nih.gov/pubmed/10062328>.
- [35] A. D. Becke, *The Journal of Chemical Physics* **98**, 5648 (1993), ISSN 00219606, URL <http://scitation.aip.org/content/aip/journal/jcp/98/7/10.1063/1.464913>.
- [36] B. O. Roos, *The Complete Active Space Self-Consistent Field Method and its Applications in Electronic Structure Calculations* (John Wiley Sons, Inc., 2007), pp. 399–445, ISBN 9780470142943, URL <http://dx.doi.org/10.1002/9780470142943.ch7>.
- [37] G. Chaban, M. W. Schmidt, and M. S. Gordon, *Theoretical Chemistry Accounts* **97**, 88 (1997), ISSN 1432-881X, URL <http://dx.doi.org/10.1007/s002140050241>.
- [38] M. Head-Gordon, J. A. Pople, and M. J. Frisch, *Chemical Physics Letters* **153**, 503

- (1988), ISSN 0009-2614, URL <http://www.sciencedirect.com/science/article/pii/0009261488852503>.
- [39] G. H. Booth, A. J. W. Thom, and A. Alavi, *The Journal of chemical physics* **131**, 054106 (2009), ISSN 1089-7690, URL <http://www.ncbi.nlm.nih.gov/pubmed/19673550>.
- [40] G. H. Booth and A. Alavi, *The Journal of chemical physics* **132**, 174104 (2010), ISSN 1089-7690, URL <http://www.ncbi.nlm.nih.gov/pubmed/20459153>.
- [41] D. Cleland, G. H. Booth, and A. Alavi, *The Journal of chemical physics* **132**, 041103 (2010), ISSN 1089-7690, URL <http://www.ncbi.nlm.nih.gov/pubmed/20113011>.
- [42] G. H. Booth, D. Cleland, A. J. W. Thom, and A. Alavi, *The Journal of chemical physics* **135**, 084104 (2011), ISSN 1089-7690, URL <http://www.ncbi.nlm.nih.gov/pubmed/21895156>.
- [43] E. Giner, A. Scemama, and M. Caffarel, *Canadian Journal of Chemistry* **91**, 879 (2013), ISSN 0008-4042, URL <http://www.nrcresearchpress.com/doi/abs/10.1139/cjc-2013-0017>.
- [44] F. Reboredo, R. Hood, and P. Kent, *Physical Review B* **79**, 195117 (2009), ISSN 1098-0121, URL <http://link.aps.org/doi/10.1103/PhysRevB.79.195117>.
- [45] M. Bajdich, M. L. Tiago, R. Q. Hood, P. R. C. Kent, and F. a. Reboredo, *Physical Review Letters* **104**, 193001 (2010), ISSN 0031-9007, URL <http://link.aps.org/doi/10.1103/PhysRevLett.104.193001>.
- [46] D. M. Cleland, G. H. Booth, and A. Alavi, *The Journal of chemical physics* **134**, 024112 (2011), ISSN 1089-7690, URL <http://www.ncbi.nlm.nih.gov/pubmed/21241085>.
- [47] The initiator approach was used in all FCIQMC calculations [46]. This leads to errors on the order of 0.1 mHa, well below the accuracy needed to benchmark QMC calculations in this article.

Acknowledgments

This work was supported through the Predictive Theory and Modeling for Materials and Chemical Science program by the Office of Basic Energy Sciences (BES), Department of Energy (DOE). This work was performed under the auspices of the US DOE by LLNL under Contract DE-AC52-07NA27344.