

Unbiasing the initiator approximation in full configuration interaction quantum Monte Carlo ^{EP}

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ABSTRACT

We identify and rectify a crucial source of bias in the initiator full configuration interaction quantum Monte Carlo algorithm. Noninitiator determinants (i.e., determinants whose population is below the initiator threshold) are subject to a systematic *undersampling* bias, which in large systems leads to a bias in the energy when an insufficient number of walkers are used. We show that the acceptance probability (p_{acc}), that a noninitiator determinant has its spawns accepted, can be used to unbias the initiator bias, in a simple and accurate manner, by reducing the applied shift to the noninitiator proportionately to p_{acc} . This modification preserves the property that in the large walker limit, when $p_{acc} \rightarrow 1$, the unbiasing procedure disappears, and the initiator approximation becomes exact. We demonstrate that this algorithm shows rapid convergence to the FCI limit with respect to the walker number and, furthermore, largely removes the dependence of the algorithm on the initiator threshold, enabling highly accurate results to be obtained even with large values of the threshold. This is exemplified in the case of butadiene/ANO-L-pVDZ and benzene/cc-pVDZ, correlating 22 and 30 electrons in 82 and 108 orbitals, respectively. In butadiene 5×10^7 and in benzene 10^8 walkers suffice to obtain an energy within a millihartree of the coupled cluster singles doubles triples and perturbative quadruples [CCSDT(Q)] result in Hilbert spaces of 10^{26} and 10^{35} , respectively. Essentially converged results require $\sim 10^8$ walkers for butadiene and $\sim 10^9$ walkers for benzene and lie slightly lower than CCSDT(Q). Owing to large-scale parallelizability, these calculations can be executed in a matter of hours on a few hundred processors. The present method largely solves the initiator-bias problems that the initiator method suffered from when applied to medium-sized molecules.

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I. INTRODUCTION

The full configuration interaction quantum Monte Carlo (FCIQMC) algorithm¹ is a projective QMC method designed to solve the electronic Schrödinger eigenvalue problem in a given basis set at the full-configuration interaction level. It is based on a population dynamics of a set of positive and negative walkers, the master equation of which is derived by interpreting the imaginary-time Schrödinger equation as a first-order kinetic equation. In the limit of a large number of walkers under steady-state conditions, the population dynamics samples the exact fermionic ground-state wavefunction. The algorithm is highly flexible, being generalizable to

a number of different types of problems, including sampling excited states of the same symmetry as the ground state,² to complex wavefunctions appropriate for solids,³ to the real-time domain for spectroscopic applications,⁴ to Jastrow-factorized explicitly correlated wavefunctions,^{5–7} and to spin-adaptation via the graphical unitary group approach.⁸ There are two forms of the algorithm: a “full” formulation in which the Hamiltonian is applied in an unconstrained form and an “initiator” approximation (i-FCIQMC)⁹ in which a constraint is applied to the Hamiltonian, to be discussed in detail later.

In its full form, FCIQMC converges without bias onto the ground-state eigenvector of a Hamiltonian, assuming it to be

nondegenerate (degenerate or near-degenerate cases are treatable via the excited-state approach). However, the full version of FCIQMC requires a minimum number of walkers to do so—simulations with insufficient numbers of walkers are unable to stably converge onto the exact solution. This number is both system and basis dependent and is usually found to be smaller than the size of the Hilbert space, implying a lower memory requirement compared to iterative exact diagonalization. However, it is also found to scale with the size of the Hilbert space (for example, as the number of electrons is increased), making it impractical for many systems of interest. In other words, the FCIQMC algorithm has an exponential scaling memory requirement, similar to that of iterative methods such as the Lanczos or Davidson algorithms.

The instability observed in the subminimum walker regime of the full FCIQMC algorithm is a manifestation of the sign-problem in this method, which has been discussed by Spencer *et al.*¹⁰ in terms of competition with the ground state of a different (sign-problem-free) Hamiltonian with off-diagonal elements given by $-|H\rangle$, the latter dominating in the subcritical walker regime. In essence, an insufficient number of walkers means that the walker annihilation events of the algorithm do not occur with sufficient frequency, and the correct permanently established sign-structure of the CI coefficients cannot emerge from the random dynamics of the method. In fact, determinants which are not permanently occupied but are only visited occasionally fluctuate in sign as they are visited by walkers of either sign. Such sign-fluctuating determinants are a source of sign-incoherent noise: their progeny also fluctuate in sign, thereby propagating this noise exponentially. In order to prevent this, in the “initiator” method, a constraint is placed on the spawning step of the algorithm. The instantaneous distribution of walkers is divided into two (dynamically evolving) sets: those walkers which reside on determinants populated by more than a certain number n_a of walkers (typically set to 3) are deemed to be “initiators.” Such determinants are deemed to have the correct sign, and they are allowed to freely spawn progeny on connected determinants, as dictated by the Hamiltonian. Those walkers which reside on determinants occupied by less than or equal to n_a walkers are designated as “noninitiators.” They are allowed to spawn progeny only on already occupied determinants (initiators or noninitiators). In other words, in the initiator approximation, certain off-diagonal Hamiltonian matrix elements of low-amplitude determinants are dynamically discarded. (The word dynamical is used to emphasize that, as the distribution of walkers changes from iteration to iteration, the discarded part of the Hamiltonian also changes. It is not a fixed set, determined *a priori* by a selection criterion.) It is found that with this modification, *stable simulations can be performed at any walker number (however small)*, thus obviating the memory bottleneck of the full algorithm. However, this comes at the cost of a systematic bias in the computed energy. This “initiator” bias can be made arbitrarily small by increasing the walker number, and indeed the algorithm is designed to revert to the “full” (i.e., exact) algorithm in the limit of a large number of walkers. In practice, for systems up to about 20 electrons, convergence can be achieved with respect to the walker number, well before memory requirements have become impractical. However, as the system size grows, it has been found that the convergence with respect to the walker number slows down such that it becomes practically impossible to converge to the exact FCI limit.

In this paper, we show that the initiator bias can be easily rectified as the simulation proceeds, enabling convergence to the FCI limit with relatively small number of walkers, several orders of magnitude fewer than that required by the initiator method or the full FCIQMC method. The methodology not only yields near-exact FCI-level energies, but also the reduced density matrices via the replica method,¹¹ which enables property calculation. The latter will be the subject of a forthcoming publication.

Recently, Blunt¹² has proposed a perturbative correction to estimate the initiator error with respect to a variational estimate of the i-FCIQMC energy obtained from the reduced density matrices. This method is in the spirit of the Epstein-Nesbet PT2 correction^{13,14} of the selected CI methods such as CIPSI,¹⁵ heat-bath CI,¹⁶ and other adaptive methods.^{17–20} These methods can be used to extrapolate to the $E_{PT2} \rightarrow 0$ limit, thereby producing estimates of the FCI energy. However, they crucially rely on efficient hybrid stochastic means to obtain the perturbative energy corrections and do not easily yield corrections to the *wavefunctions* without the substantial computational overhead. This makes the calculation of properties at the corresponding level of accuracy (i.e., approaching FCI) very difficult.

Ten-no²¹ has discussed the initiator approximation in terms of size inconsistency error and has proposed several ways to mitigate this via coupled electron pair type approximations. The method proposed here has a resemblance to these concepts, but the form of the correction is different, being adapted to each noninitiator determinant rather than prescribed, and vanishes in the larger walker limit, thereby ensuring exactness in that limit.

Incremental many-body expansions (MBEs) of FCI^{22–24} offer an alternative approach to the FCI problem but do involve a large number of subspace CASCI diagonalization, which for large systems may become too large for deterministic diagonalization. In such problems, the method to be discussed below could be used in conjunction with MBE-type methods to alleviate those bottlenecks.

Another highly promising approach that could benefit from the present methodology is the cluster-analysis-driven (CAD) FCIQMC methodology of Piecuch and co-workers,^{25,26} who solve the CCSD amplitude equations in the presence of the T_3 and T_4 amplitudes extracted from FCIQMC propagations. If the T_3 and T_4 amplitudes are exact, the resulting energies from these equations are also exact (i.e., equivalent to FCI). Piecuch *et al.* have demonstrated this for small systems such as the water molecule, yielding exact energies from information derived from relatively short FCIQMC propagations. The present methodology may be a route to the accurate T_3 and T_4 amplitudes at an affordable cost for larger systems and would result in a very powerful combination of the coupled cluster theory and FCIQMC.

The structure of this paper is as follows: We first review the initiator FCIQMC method and identify a source of bias which results from the initiator approximation. We then discuss a method which we call the *adaptive-shift method* to unbias for this error on the fly and discuss its implementation. Next, we show how this method works in the case of butadiene and benzene in double-zeta basis sets. We end with some concluding remarks on future perspectives.

II. THE INITIATOR AND ADAPTIVE SHIFT METHODS

We begin by reviewing the main concepts behind FCIQMC and i-FCIQMC algorithms. The imaginary-time Schrödinger equation for the wavefunction Ψ is as follows:

$$-\partial_t \Psi = (\hat{H} - E)\Psi = 0. \quad (1)$$

Ψ is expanded in an FCI basis,

$$\Psi = \sum_i c_i |D_i\rangle, \quad (2)$$

where the coefficients c_i are to be determined to achieve the stationarity condition implied by Eq. (1). In FCIQMC, in its original formulation, a distribution of N_w signed walkers $\{i_1, i_2, \dots, i_y, \dots, i_{N_w}\}$ of unit amplitude ($\{s_y = \pm 1\}$, $N_w = \sum_y |s_y|$) is invoked such that c_i coefficients are given via the relation

$$c_i \propto \sum_y s_y \delta(i_y - i) \equiv N_i. \quad (3)$$

In a subsequent development of FCIQMC,^{27,28} the weights s_y were generalized to floating point numbers with the condition $|s_y| \geq s_{cut}$, where s_{cut} denotes the minimum amplitude of a walker, here taken to be 1. This modification allows for a much finer resolution of the instantaneous wavefunction to be achieved without permanent storage of excessively small determinant weights and leads to faster convergence with population and smoother convergence with imaginary time. This version of the algorithm, as implemented in the NECI code²⁹ with floating point walker weights, is the one we will employ in this study.

According to Eqs. (1) and (3), c_i is proportional to the signed number of walkers, N_i , on determinant $|D_i\rangle$. The walker population dynamics is governed by

$$-\partial_t N_i = (H_{ii} - (E_{HF} + S))N_i + \sum_{j \neq i} H_{ij} N_j, \quad (4)$$

where S is the applied shift, which at convergence (keeping the number of walkers fixed) equals the exact correlation energy. The population dynamics is implemented via the three FCIQMC steps of spawning, diagonal death, and walker annihilation. For more details, the reader is referred to Ref. 1. In practice, a time-average can be taken in the long-time limit so that $c_i \propto \langle N_i \rangle_t$.

In the initiator method, the master equation is modified as follows:

$$-\partial_t N_i = (H_{ii} - (E_{HF} + S))N_i + \sum_{j \neq i} \hat{H}_{ij}(N_i, N_j)N_j, \quad (5)$$

where

$$\hat{H}_{ij}(N_i, N_j) = \begin{cases} H_{ij}, & \text{if } |N_j| > n_a \text{ or } N_i \neq 0, \\ 0, & \text{otherwise.} \end{cases} \quad (6)$$

\hat{H} is the population-dependent truncated Hamiltonian. In practice, the initiator algorithm is implemented as follows: for a noninitiator determinant, say i , an attempt is made to spawn onto *any* of its connected determinants, say j , with the probability proportional to H_{ij} . *If j is found to be empty, the move is rejected.* The initiator rule therefore suppresses spawning events from low-amplitude determinants (the noninitiators) onto empty sites. If these are not suppressed

(as in the full method), it is found that there is an extremely rapid, exponential increase in walker population which is difficult to control (until the annihilation events become sufficiently frequent to counter this rapid exponential growth). It is important to note that all spawns onto occupied sites are, however, allowed, and therefore, the initiator modification to the Hamiltonian is quite subtle and dynamic: as the number of walkers increases, an increasing amount of the Hilbert space becomes populated, and as a result, there are fewer initiator-rule rejections. On the other hand, for not very large walker populations, it is typically found that the majority of noninitiator spawns are disallowed (rejected Monte Carlo moves) because for a typical noninitiator, the number of occupied neighboring determinants (its local Hilbert space) is quite sparsely populated. As a result, many Hamiltonian matrix elements belonging to a noninitiator determinant are effectively zeroed, meaning that the local Hilbert space is underpopulated, as compared to what it would be if the fully unconstrained Hamiltonian was to be applied. This leads to an undersampling bias since the *feedback* from the local Hilbert space onto the determinant is also smaller than it should be. This is the bias we wish to rectify.

To account for this bias, we now modify the shift applied to a noninitiator determinant such that instead of applying the full shift S , we apply a *local* shift S_i , appropriate for that determinant,

$$S_i = S \times p_{acc}[D_i], \quad (7)$$

where $p_{acc}[D_i]$ is measured in the simulation itself by monitoring the fraction of spawns from $|D_i\rangle$ that have been accepted or rejected owing to the initiator rule. In other words, the master equation for a noninitiator is modified as follows:

$$-\partial_t N_i = (H_{ii} - (E_{HF} + S_i))N_i + \sum_{j \neq i} \hat{H}_{ij}(N_i, N_j)N_j. \quad (8)$$

This equation defines the *adaptive-shift* method, in which the shift being applied to noninitiators is modified (reduced) according to the rejection probabilities of attempted spawns. In order to obtain $p_{acc}[D_i]$, we accumulate two sums, over the accepted (A_i) and rejected (R_i) spawns, respectively, from D_i ,

$$A_i = \sum_{j \in \text{accepted}} w_{ij}, \quad (9)$$

$$R_i = \sum_{j \in \text{rejected}} w_{ij}, \quad (10)$$

$$p_{acc}[D_i] = \frac{A_i}{A_i + R_i}, \quad (11)$$

where w_{ij} is the weight to be assigned for each attempted $i \rightarrow j$ spawn, whose form will be derived shortly from the perturbation theory. For the moment, let us note that if the determinant $|D_i\rangle$ becomes an initiator, the full shift is applied since in that case $R_i = 0$ and therefore, $p_{acc}[D_i] = 1$. Similarly, as the number of walkers N_w increases, the local Hilbert space surrounding D_i becomes populated, and in that case also $p_{acc} \rightarrow 1$, i.e.,

$$\lim_{N_w \rightarrow \infty} p_{acc}[D_i] = 1 \text{ for all } i. \quad (12)$$

The full master equation of FCIQMC is therefore reobtained in the large walker limit.

The simplest choice to make for the weights, w_{ij} , is to set them all to be unity. This choice is actually acceptable, in which it ensures the crucial limit of Eq. (12). However, it ignores the fact that not all determinants j in the local Hilbert space of i can be expected to have equal weight, especially in *ab initio* Hamiltonians where the different j can be coupled to i with nonuniform matrix element magnitudes $|H_{ij}|$ and also can have strongly varying local energies H_{jj} . To take into account the expected nonuniformity in the importance of the determinants in the local Hilbert space of i , we can appeal to the concepts behind Löwdin downfolding.³⁰ In that procedure, if a determinant j is to be downfolded into i , then the off-diagonal Hamiltonian matrix element H_{ij} is zeroed, and the diagonal matrix element H_{ii} is changed by $H_{ij}^2/(E_0 - H_{jj})$, where E_0 is the exact energy. This therefore constitutes an effective reduction in the energy of i . This is a second-order perturbation theory argument: $H_{ij}/(E_0 - H_{jj})$

represents the first-order perturbative amplitude of D_j due to D_i , and the further factor of H_{ij} represents the feedback from D_j to D_i . The overall effect is then the well-known perturbation expression. Garniron *et al.*³¹ have recently used a similar argument to dress effective Hamiltonians obtained within a CIPSI selected-CI approach.

Motivated by this perturbation theory argument, we define w_{ij} , the weight assigned to the attempted spawn on D_j from D_i , to be as follows:

$$w_{ij} = \frac{|H_{ij}|}{H_{jj} - E_0}. \quad (13)$$

Physically, this is the neglected amplitude on D_j due to a walker on D_i based on the perturbation theory. Although as an estimate of the neglected amplitude, this cannot be exact, in practice,

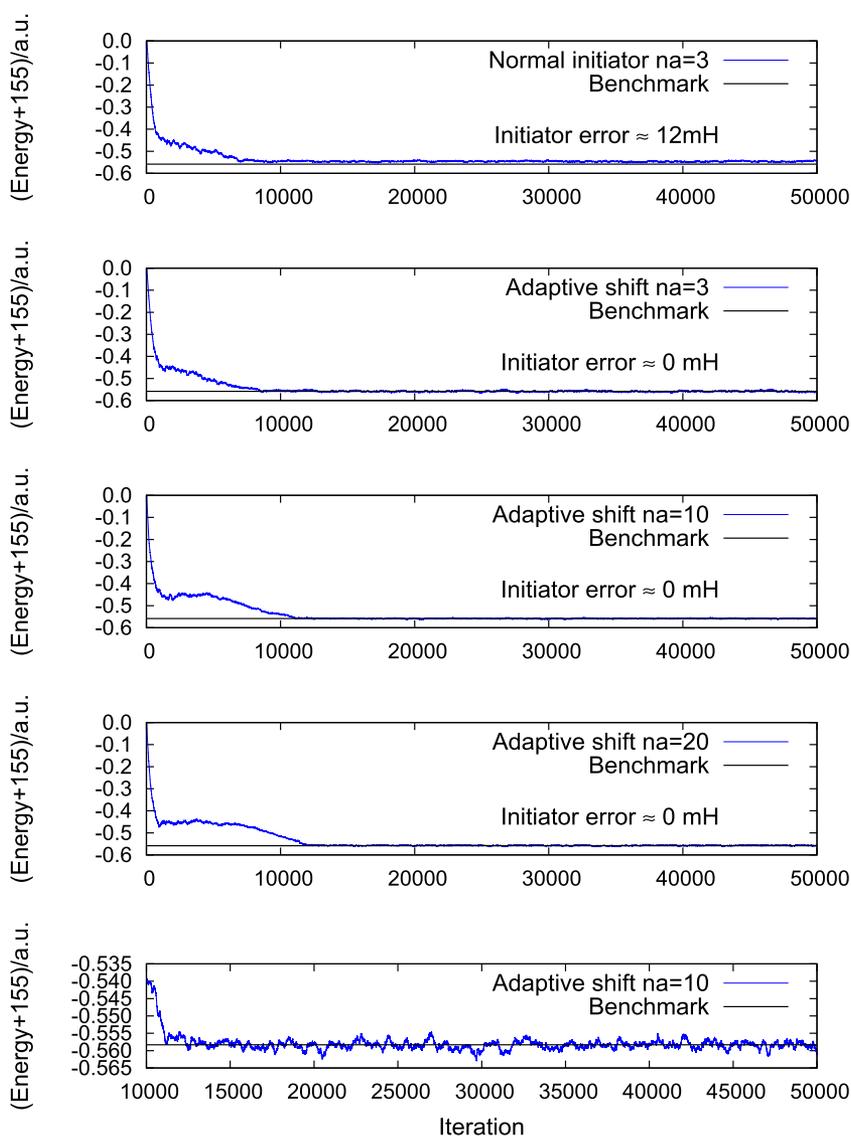


FIG. 1. Total energy trajectories of 100M walker FCIQMC simulations of butadiene/ANO-L-pVDZ, using the standard initiator (top panel) and the adaptive shift method (2nd, 3rd, and 4th panels with $n_a = 3, 10,$ and $20,$ respectively). The 5th panel is a zoom-in of the $n_a = 10$ simulation. The extrapolated HCIPT2 result of -155.5582 is used as the benchmark.

the errors made by the perturbation theory estimate are largely inconsequential since the unbiasing procedure is constructed to become small and eventually disappear in the large walker limit.

From an implementation point of view, this form of w_{ij} imposes a small overhead compared to a standard initiator algorithm since the energy H_{jj} of the determinant D_j of an attempted spawn must be calculated even if the move is going to be rejected (in the standard algorithm, H_{jj} is calculated only if the spawn onto D_j is accepted). However, this overhead turns out to be negligible compared with the benefits of the methodology in terms of speed of convergence with respect to the walker number.

III. RESULTS

A. Butadiene

We first apply the adaptive-shift FCIQMC method to the butadiene molecule in an ANO-L-pVDZ basis (22 electrons in 82 orbitals), which has proven challenging for the normal initiator method. For example, initiator calculations with 10^9 walkers with the conventional method yielded an energy of $-155.5491(4)$ a.u.,³² which is some 8 mhartree above a DMRG calculation (-155.5573) obtained with a large (6000) number of renormalized functions.³³ While the exact energy for this system is not known, it can be expected to be only slightly lower than this, most likely within a millihartree, and other highly accurate methods are consistent with this: CCSDT(Q) yields -155.55756 and CCSDTQ -155.55738 , while extrapolated HCIPT2 yields $-155.5582(1)$.³⁴

For the present study, as in the original study,³² restricted Hartree-Fock (HF) orbitals were used. The calculations were done by starting 100 walkers on the HF determinant and growing the population (using $S = 0$) until N_w reached the target population, after which the shift was allowed to vary in the adaptive shift mode. The target populations were set to 10M, 50M, 100M, and 200M walkers. (In the final case, the 200M walker simulations were grown from the equilibrated 100M walker simulations.) In order to assess the dependence of the results on the initiator parameter n_a , three independent sets of calculations were performed, using $n_a = 3, 10,$ and 20 . The calculations were run for 50 000 time steps, using a time set of $\Delta\tau = 10^{-3}$ a.u. We used a semistochastic space²⁷ of $|\mathcal{D}| = 10^3(10^4)$ for the systems up to 100M (200M) walkers, selected from the most

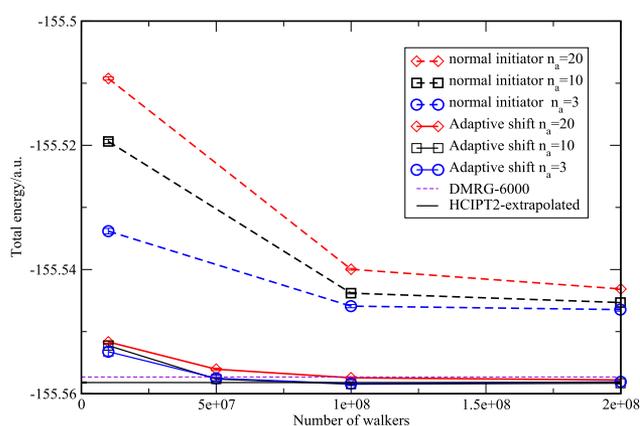


FIG. 2. Total energies of butadiene/ANO-L-pVDZ for both normal initiator and adaptive shift methods, as a function of the number of walkers, for three values of the initiator parameter n_a .

populated determinants 1000 time steps after the variable shift mode had been reached, this being the (“pops-core”) protocol in the NECI code.²⁸ A trial wavefunction space of $|T| = 10$ of the leading determinants was also used to compute projected energies. For systems dominated by one determinant, as in the present case, the results obtained from projections on the Hartree-Fock determinant and the trial wavefunction are found to be very similar. For example, at 200M walkers with $n_a = 10$, the trial wavefunction and the HF projected energy both yield an energy of $-155.5583(2)$, i.e., in agreement down to a stochastic error of 0.2 mhartree. Similar (albeit very slightly worse) agreement is found in the smaller 10M walker simulation [$-155.5523(3)$ and $-155.5524(4)$ for the trial and HF-projected wavefunctions, respectively]. For consistency, all results reported below will be based on the trial wavefunction projected energies.

As a control, a similar set of calculations were run in the normal initiator mode (at target populations 10M, 100M, and 200M), with the three values of the initiator parameter.

Trajectories of the calculations are shown in Fig. 1, for the standard initiator and adaptive shift methods, for different values

TABLE I. Butadiene total energy in a.u. (offset by 155 a.u.).

$N_w/10^6$	Initiator			Adaptive shift		
	$n_a = 3$	$n_a = 10$	$n_a = 20$	$n_a = 3$	$n_a = 10$	$n_a = 20$
10	$-0.5338(4)$	$-0.5194(3)$	$-0.5092(3)$	$-0.5532(7)$	$-0.5523(3)$	$-0.5517(2)$
50				$-0.5575(5)$	$-0.5577(3)$	$-0.5555(2)$
100	$-0.5459(2)$	$-0.5438(1)$	$-0.5399(2)$	$-0.5583(3)$	$-0.5584(2)$	$-0.5574(2)$
200	$-0.5465(2)$	$-0.5453(1)$	$-0.5431(1)$	$-0.5581(2)$	$-0.5583(2)$	$-0.5578(2)$
CCSD(T)						-0.5550
CCSDT(Q)						-0.5576
DMRG-6000						-0.5573
HCIPT2 (extrap)						$-0.5582(1)$

of n_a . In all cases, the simulations converge from the Hartree-Fock determinant to their equilibrium steady-state distribution within $\sim 10\,000$ iterations (i.e., 10 a.u. of imaginary time) and are thereafter stable, exhibiting small fluctuations of a few millihartree. However, it is evident that the standard initiator method incurs a noticeable bias relative to the benchmark, whereas the three adaptive runs, with the very different values of the initiator threshold, all agree extremely well with the benchmark. The larger values of n_a tend to exhibit smaller fluctuations in the projected energy. This is because with the larger values of n_a , the reference (HF) population, as well as those of the singles and doubles, tends to be higher than when small n_a is used, leading to smaller fluctuations in the projected energy.

The full results of the butadiene simulations are shown in Table I and in Fig. 2. It is clear that the adaptive shift

simulations, irrespective of the value of the initiator parameter used, converge to a narrow range of energies ranging from $-155.5578(2)$ to $-155.5583(2)$, which are in very good agreement with the benchmark value. The fact that the result is largely independent of the initiator value is remarkable; the different values of the initiator parameter lead to calculations with very different number of initiators in the simulations: for example, at 200M walkers, the $n_a = 3$ simulation has 6×10^5 initiator determinants, while the $n_a = 20$ simulation has 5×10^4 , an order of magnitude fewer. Yet the fact that the projected energies are essentially independent of this implies that the adaptive shift method is correctly removing the undersampling bias of each noninitiator so that the ratio of the amplitude of a given noninitiator to the reference determinant is correct, this being the necessary requirement to obtain the exact energy.

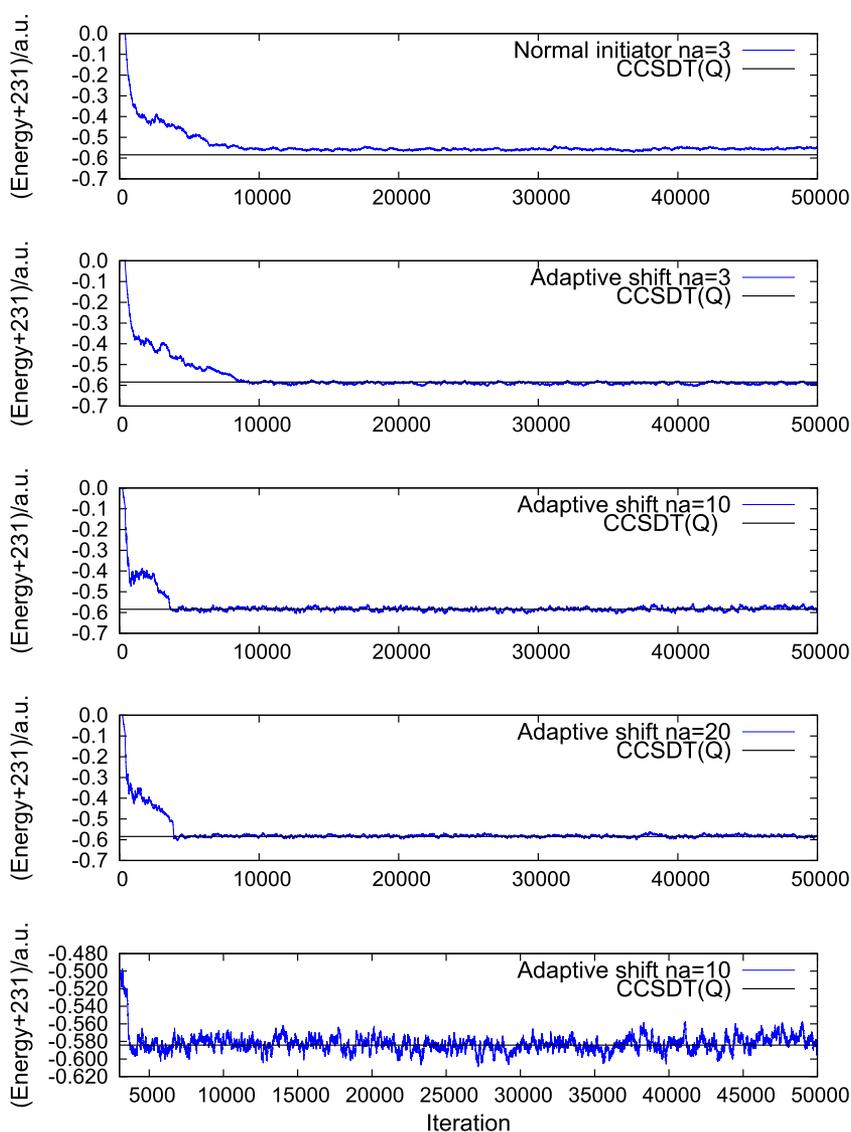


FIG. 3. Total energy trajectories of 100M walker FCIQMC simulations of benzene/cc-pVDZ, using the standard initiator (top panel) and adaptive shift method (2nd, 3rd, and 4th panels with $n_a = 3, 10,$ and 20 , respectively). The 5th panel is a zoom-in of the $n_a = 10$ simulation.

B. Benzene

Next, we report adaptive shift calculations on the ground state of the benzene molecule in a cc-pVDZ basis (30 electrons in 108 orbitals) at the experimental geometry given on the NIST website (see the [supplementary material](#)). In a D_{2h} point group, the Hilbert space is $\sim 10^{35}$. CASSCF(6,12) orbitals were used, as in a previous study using linearized coupled cluster theory.³⁵ Similar to the butadiene calculations, calculations were performed at three values of the initiator parameter, $n_a = 3, 10,$ and 20 , with walkers in the range 100M to 1.6B. The semistochastic and trial-wavefunction spaces were also similarly chosen. Trajectories of the 100M walker simulations are shown in [Fig. 3](#). The behavior observed for this much larger system is similar to that of butadiene, with a noticeable initiator bias in the normal initiator method (~ 20 mhartree at 1.6B walkers at $n_a = 3$) and a much reduced error in the adaptive shift simulations. The complete results are shown in [Fig. 4](#). It is seen that even with 10^8 walkers, excellent energies are obtained, $-231.589(1)$ at $n_a = 3$, $-231.5833(7)$ at $n_a = 10$, and $-231.5818(2)$ at $n_a = 20$, to be compared with the CCSDT(Q) value (-231.58416). Compared to the butadiene simulation, the fluctuations in the instantaneous projected energy are somewhat larger, about 20 mhartree rather than 5 mhartree, but given the much larger size of the problem with increased connectivity around each determinant of a factor of ~ 4 , this is not surprising. As the walker number is increased to 1.6B, these numbers converge into a narrower range of less than 1.6 mhartree: $-231.5858(2)$ at $n_a = 3$, $-231.5853(6)$ at $n_a = 10$, and $-231.5841(3)$ at $n_a = 20$. The main difference observed here, compared to butadiene, is that the $n_a = 3$ simulation converges from below, with an overshoot of about 4 mhartree before rising to the above value. The two larger initiator parameters potentially also exhibit overshoots, but these are much smaller, about 1 mhartree, and well within the stochastic fluctuations of simulation, as demonstrated in the zoom-in of the $n_a = 10$ simulation [Fig. \(3\)](#). Overall, it is difficult to pinpoint the energy with higher accuracy than 1 mhartree, and we would suggest that the exact answer lies within a mhartree of -231.585 , which is consistent with the CCSDT(Q)

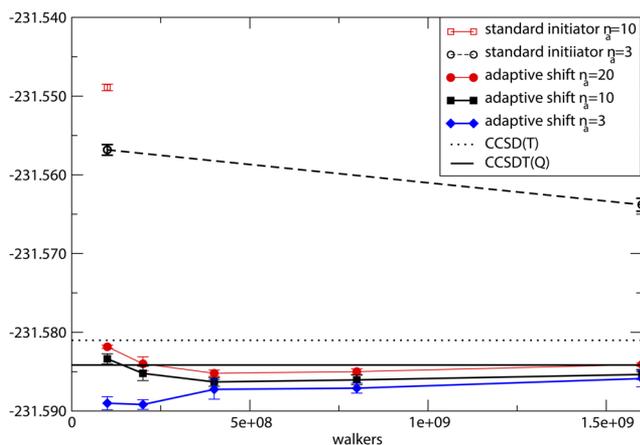


FIG. 4. Total energy of benzene/cc-pVDZ with the walker number for different initiator parameters, for the standard initiator and adaptive shift methods.

energy of -231.58416 . Normally for such systems dominated by dynamical correlation, the CC hierarchy converges from above, and our best estimate of -231.585 is indeed slightly below the CCSDT(Q) value.

IV. CONCLUDING REMARKS

In conclusion, we have demonstrated an adaptive-shift method to unbiased the initiator bias on the fly in an i-FCIQMC calculation, resulting in highly accurate simulations of sizeable systems such as benzene/cc-pVDZ. Near-FCI quality energies can be obtained with drastically reduced number of walkers as compared to the standard initiator method. The internal consistency of the methodology is demonstrated by the fact that the dependence of the method on the initiator parameter is largely removed, enabling converged results to be obtained even with large values of the initiator parameter. The advantage of using a large initiator parameter is that the reference population is much larger, leading to smaller fluctuations in the simulations. The latter will prove very useful in multireference systems, where populations on the reference determinants tend to be small and require large initiator thresholds for stabilization. The fact that we can now correctly unbiased the simulations even when the initiator threshold is large will be extremely beneficial in the treatment of strongly correlated, multireference systems, which we will return to in subsequent work. In addition, in contrast to methods which rely on extrapolations of the FCI limit to achieve accuracy, the present method yields near-exact density matrices, which can be used to calculate properties. This will be the subject of a forthcoming publication.

SUPPLEMENTARY MATERIAL

The geometry of the benzene molecule used in this study is specified in the [supplementary material](#) file.

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REFERENCES

- 1 G. H. Booth, A. J. W. Thom, and A. Alavi, *J. Chem. Phys.* **131**, 054106 (2009).
- 2 N. S. Blunt, S. D. Smart, G. H. Booth, and A. Alavi, *J. Chem. Phys.* **143**, 134117 (2015).
- 3 G. H. Booth, A. Grüneis, G. Kresse, and A. Alavi, *Nature* **493**, 365 (2013).
- 4 K. Guthier, W. Dobrautz, O. Gunnarsson, and A. Alavi, *Phys. Rev. Lett.* **121**, 056401 (2018).
- 5 H. Luo and A. Alavi, *J. Chem. Theory Comput.* **14**, 1403 (2018).
- 6 W. Dobrautz, H. Luo, and A. Alavi, *Phys. Rev. B* **99**, 075119 (2019).
- 7 A. J. Cohen, H. Luo, K. Guthier, W. Dobrautz, D. P. Tew, and A. Alavi, *J. Chem. Phys.* **151**, 061101 (2019).
- 8 W. Dobrautz, S. D. Smart, and A. Alavi, *J. Chem. Phys.* **151**, 094104 (2019).
- 9 D. Cleland, G. H. Booth, and A. Alavi, *J. Chem. Phys.* **132**, 041103 (2010).
- 10 J. S. Spencer, N. S. Blunt, and W. M. Foulkes, *J. Chem. Phys.* **136**, 054110 (2012).
- 11 C. Overy, G. H. Booth, N. S. Blunt, J. J. Shepherd, D. Cleland, and A. Alavi, *J. Chem. Phys.* **141**, 244117 (2014).
- 12 N. S. Blunt, *J. Chem. Phys.* **148**, 221101 (2018).
- 13 Y. Garniron, A. Scemama, P.-F. Loos, and M. Caffarel, *J. Chem. Phys.* **147**, 034101 (2017).

- ¹⁴S. Sharma, A. A. Holmes, G. Jeanmairet, A. Alavi, and C. J. Umrigar, *J. Chem. Theory Comput.* **13**, 1595 (2017).
- ¹⁵B. Huron, J. P. Malrieu, and P. Rancurel, *J. Chem. Phys.* **58**, 5745 (1973).
- ¹⁶A. Holmes, N. Tubman, and C. Umrigar, *J. Chem. Theory Comput.* **12**, 3674 (2016).
- ¹⁷F. A. Evangelista, *J. Chem. Phys.* **140**, 124114 (2014).
- ¹⁸N. M. Tubman, J. Lee, T. Y. Takeshita, M. Head-Gordon, and K. B. Whaley, *J. Chem. Phys.* **145**, 044112 (2016).
- ¹⁹J. B. Schriber and F. A. Evangelista, *J. Chem. Phys.* **144**, 161106 (2016).
- ²⁰W. Liu and M. R. Hoffmann, *J. Chem. Theory Comput.* **12**, 1169 (2016).
- ²¹S. L. Ten-no, *J. Chem. Phys.* **147**, 244107 (2017).
- ²²J. J. Eriksen, F. Lipparini, and J. Gauss, *J. Phys. Chem. Lett.* **8**, 4633 (2017).
- ²³J. J. Eriksen and J. Gauss, e-print [arXiv:1910.03527](https://arxiv.org/abs/1910.03527) (2019).
- ²⁴P. M. Zimmerman, *J. Chem. Phys.* **146**, 104102 (2017).
- ²⁵J. E. Deustua, I. Magoulas, J. Shen, and P. Piecuch, *J. Chem. Phys.* **149**, 151101 (2018).
- ²⁶J. E. Deustua, S. H. Yuwono, J. Shen, and P. Piecuch, *J. Chem. Phys.* **150**, 111101 (2019).
- ²⁷F. R. Petruzielo, A. A. Holmes, H. J. Changlani, M. P. Nightingale, and C. J. Umrigar, *Phys. Rev. Lett.* **109**, 230201 (2012).
- ²⁸N. S. Blunt, S. D. Smart, J. A. F. Kersten, J. S. Spencer, G. H. Booth, and A. Alavi, *J. Chem. Phys.* **142**, 184107 (2015).
- ²⁹G. H. Booth, S. D. Smart, and A. Alavi, *Mol. Phys.* **112**, 1855 (2014).
- ³⁰P. Lowdin, *J. Chem. Phys.* **19**, 1396 (1951).
- ³¹Y. Garniron, A. Scemama, E. Giner, M. Caffarel, and P.-F. Loos, *J. Chem. Phys.* **149**, 064103 (2018).
- ³²C. Daday, S. Smart, G. H. Booth, A. Alavi, and C. Filippi, *J. Chem. Theory Comput.* **8**, 4441 (2012).
- ³³R. Olivares-Amaya, W. Hu, N. Nakatani, S. Sharma, J. Yang, and G. K.-L. Chan, *J. Chem. Phys.* **142**, 034102 (2015).
- ³⁴A. D. Chien, A. A. Holmes, M. Otten, C. J. Umrigar, S. Sharma, and P. M. Zimmerman, *J. Phys. Chem. A* **122**, 2714 (2018).
- ³⁵G. Jeanmairet, S. Sharma, and A. Alavi, *J. Chem. Phys.* **146**, 044107 (2017).