Selected configuration interaction wave functions in phaseless auxiliary field quantum Monte Carlo

Ankit Mahajan,1,∗ Joonho Lee,2 and Sandeep Sharma1†

1Department of Chemistry, University of Colorado, Boulder, CO 80302, USA
2Department of Chemistry, Columbia University, New York, New York 10027, USA

We present efficient algorithms for using selected configuration interaction (sCI) trial wave functions in phaseless auxiliary field quantum Monte Carlo (ph-AFQMC). These advancements, geared towards optimizing computational performance for longer CI expansions, allow us to use up to a million configurations feasibly in the trial state for ph-AFQMC. In one example, we found the cost of ph-AFQMC per sample to increase only by a factor of about 3 for a calculation with $10^4$ configurations compared to that with a single one, demonstrating the tiny computational overhead due to a longer expansion. This favorable scaling allows us to study the systematic convergence of the phaseless bias in AFQMC calculations with an increasing number of configurations and provides a means to gauge the accuracy of ph-AFQMC with other trial states. We also show how the scalability issues of sCI trial states for large system sizes could be mitigated by restricting them to a moderately sized orbital active space and leveraging the near-cancellation of out of active space phaseless errors.

1. INTRODUCTION

Quantum Monte Carlo (QMC) is a powerful tool in our arsenal to tackle the quantum many-body problem. Among various QMC approaches, phaseless auxiliary-field quantum Monte Carlo (ph-AFQMC) has emerged as an accurate and efficient method. While originally from the condensed matter community (therein usually referred to as constrained-path AFQMC), ph-AFQMC has gained popularity in chemistry in recent years. The accuracy and scalability of ph-AFQMC are determined in large part by the choice of the trial wave function. The use of a trial wave function becomes necessary for retaining statistical efficiency (in sample complexity) to control the fermionic phase (or sign) problem. The constraint imposed to control the phase problem is called the phaseless approximation. When the trial wave function approaches the exact ground state, the corresponding ph-AFQMC energy tends to the ground state energy. The commonly used trial wave function for ph-AFQMC is the broken-symmetry Hartree-Fock (HF) wave function. It scales as $O(N^3)$ to obtain the trial wave function and $O(N^5)$ to perform the ph-AFQMC calculation with the trial to obtain energy for a fixed statistical error, where $N$ is the system size. Beyond HF, one may try to use a single determinant trial using approximate Bruckner orbitals, which essentially keeps the same computational scaling for ph-AFQMC. While single determinant trial wave functions are attractive due to their scalability, their accuracy can be limited and questionable in many examples.

On the other hand, there has been a flurry of developments in selected configuration interaction (sCI) methods in the last few years. Despite their steep (formally exponential) scaling with system size, sCI methods have increasingly been employed to study moderately sized systems and perform large active space correlated calculations. These methods have the capability of generating systematically more accurate approximations to the state of interest by increasing the number of configurations judiciously. This attractive feature makes sCI wave functions natural candidates for trial states in projection QMC methods. Based on significant advances in real-space QMC algorithms with such trial states, several papers have already reported calculations with long sCI expansions in diffusion Monte Carlo. There has also been some recent progress for using them in ph-AFQMC, but the commonly used algorithm based on the Sheman-Morrison-Woodbury identity has an inherent computational bottleneck with the local energy evaluation scaling as $O(N_{c}N^4)$, where $N_{c}$ is the number of determinants. This steeper scaling compared to real-space methods is due to the Gaussian orbital representation of the electron repulsion interaction. Furthermore, the force bias evaluation scales as $O(N_{c}N^3)$, which can be expensive since it is performed once every time step. Due to these, it has been challenging to scale up the ph-AFQMC calculations beyond 100-1000 configurations.

In this work, we propose to use one of the sCI methods, heat-bath CI (HCl), to generate a large trial with up to $10^6$ configurations. We then combine several algorithmic advances made by two of us using the generalized Wick’s theorem and make further improvements to accelerate ph-AFQMC calculations with a large trial. In particular, in our new algorithm, the local energy evaluation scales as $O(N_{c}N + N^4)$, and the force bias evaluation scales as $O(N_{c} + N^3)$. To alleviate the scaling issues of sCI wave functions, we study the efficacy of active space trial states in calculating energy differences and properties. The active space size is another variable to converge the phaseless error systematically in larger systems while keeping the calculation cost manageable. We use the new algorithm for ph-AFQMC with HCl trials to investigate the behavior of the phaseless bias as a function of the number of configurations in the trial for several challenging systems.

This paper is organized as follows: we first review the
ph-AFQMC algorithm (Section 2), we then discuss how once can drastically speed up the evaluation of force bias and local energy of sCI trials using the generalized Wick’s theorem (Section 3), we present results that show how phaseless errors in the ground state energy and dipole moments change as a function of the number of determinants in hydrogen chains, transition metal oxides, and a few small molecules (Section 4), and we finally conclude (Section 5).

2. PHASELESS AUXILIARY FIELD QUANTUM MONTE CARLO

We briefly summarize the procedure for phaseless AFQMC here and refer the reader to reference [16] for more details. Consider the \textit{ab initio} Hamiltonian given by

\[ \hat{H} = \sum_{ij} h_{ij} \hat{a}_i^\dagger \hat{a}_j + \frac{1}{2} \sum_{ij} \left( \sum_{\gamma} L_{ij}^\gamma \hat{a}_i^\dagger \hat{a}_j \right)^2, \]

where \( h_{ij} \) are one-electron integrals and \( L_{ij}^\gamma \) are Cholesky decomposed two-electron integrals in an orthonormal orbital basis. We will use letters \( N, M, \) and \( X \) to denote the number of electrons, number of orbitals, and number of Cholesky vectors, respectively. We note that in chemical systems, empirically, \( X \sim O(M) \) with a proportionality constant usually smaller than 10. AFQMC uses the exponential form of the projector to converge to the ground state of the Hamiltonian as

\[ e^{-\tau \hat{H}} |\psi_0\rangle \xrightarrow{\tau \to \infty} |\Psi_0\rangle, \]

where \( \tau \) is the imaginary time, \( |\Psi_0\rangle \) is the ground state, and \( |\psi_0\rangle \) is an initial state such that \( \langle \psi_1 | \psi_0 \rangle \neq 0 \). Using the Hubbard-Stratonovic transform, the short-time exponential projector can be written as

\[ e^{-\Delta \tau \hat{H}} = \int dx p(x) \hat{B}(x), \]

where \( x \) is the vector of auxiliary fields (one scalar field per Cholesky component), \( p(x) \) is the standard normal Gaussian distribution of the auxiliary fields, and \( \hat{B}(x) \) is a complex propagator given by the exponential of a one-body operator. Due to Thouless’ theorem, \( \hat{B}(x) \) acts on a Slater determinant \( |\phi\rangle \) as

\[ \hat{B}(x) |\phi\rangle = |\phi(x)\rangle, \]

where \( |\phi(x)\rangle \) is another Slater determinant obtained by a linear transformation of the orbitals in \( |\phi\rangle \). By importance sampling the auxiliary fields in equation (3) and applying the short time propagator sufficiently many times, we get a stochastic representation of the ground state wave function in the long time limit as

\[ |\Psi_0\rangle \propto \sum_i w_i \frac{|\phi_i\rangle}{\langle \psi_T | \phi_i \rangle}, \]

where \( w_i \) are weights, \( |\phi_i\rangle \) are Slater determinants with complex orbitals obtained from the orbital transformations sampled during propagation, and \( |\psi_T\rangle \) is the trial state used for importance sampling. More accurate trial states lead to less noisy weights. We use the hybrid approximation in this paper, which avoids the expensive calculation of local energy at each propagation step. Importance sampling in AFQMC involves shifting the sampled auxiliary fields by the force bias given as

\[ \bar{x}_\gamma = -\sqrt{\Delta \tau} \frac{\langle \psi_T | \sum_j L_{ij}^\gamma \hat{a}_i^\dagger \hat{a}_j |\phi\rangle}{\langle \psi_T | \phi \rangle}, \]

where \( |\phi\rangle \) is the walker. The force bias can be thought of as a dynamic correction to the mean-field contour shift that vanishes as \( \Delta \tau \to 0 \). Force bias is not enough, by itself, to control the large fluctuations stemming from the phase problem. The phaseless constraint can be used to overcome the phase problem at the expense of a systematic bias in the sampled wave function. The size of this phaseless bias is dictated by the accuracy of the trial state.

After an equilibration time, the energy of the sampled wave function can be measured as

\[ E \approx \sum_i w_i E_L(\phi_i), \]

where

\[ E_L(\phi_i) = \frac{\langle \psi_T | \hat{H} |\phi_i\rangle}{\langle \psi_T | \phi_i \rangle} \]

is the local energy of the walker \( |\phi_i\rangle \). We note that this estimator has a zero-variance property i.e. in the limit that the trial state is the exact, ground state the variance of the estimator vanishes. In practice, this means that more accurate trial states lead to less noisy local energy values.

It is evident that more accurate trial states lead to less noisy simulations and smaller phaseless biases. But, in general, the use of more sophisticated trial states comes at the expense of greater computational cost. In the following section, we present efficient algorithms to calculate force bias and local energy of sCI trial states.

3. SELECTED CONFIGURATION INTERACTION TRIAL STATES

A selected CI wave function is given by

\[ |\psi_T\rangle = \sum_n c_n |\psi_n\rangle = \sum_n c_n \prod_{\mu} \hat{a}^\dagger_{n\mu} \hat{a}_{n\mu} |\psi_0\rangle, \]

where \( |\psi_n\rangle \) are configurations obtained by particle-hole excitations from the reference configuration \( |\psi_0\rangle \), \( N_c \) is the number of configurations in the expansion, \( c_n \) are real expansion coefficients, and \( k_n \) are the excitation ranks.
We will use the indices $p_i$ and $t_j$ to denote occupied and virtual orbitals, respectively, whereas indices $i, j, \ldots$ will be used for general orbitals. The orthonormal orbital basis set used in the expansion can be chosen to be natural orbitals obtained from an HCl calculation or can be optimized using a self-consistent procedure. In the following, we use the same basis set to express the Hamiltonian in equation [4] and, in general, all second-quantized operators refer to this basis. In our prior work, we have proposed efficient algorithms for using selected CI states in variational Monte Carlo and free projection AFQMC. These focused on the calculation of local energy using the generalized Wick’s theorem. Here, we discuss an algorithm for calculating the force bias required in ph-AFQMC and briefly summarize the calculation of local energy.

### 3.1. Force bias

Calculation of the force bias for importance sampling is one of the computationally intensive parts of propagation in ph-AFQMC. Substituting the sCI trial state into the force bias expression in equation [4] we get

$$
\bar{x}_{ij} = -\sqrt{\Delta t} \sum_n \sum_{ij} c_n L_{ij} \langle \psi_n | \hat{a}^\dagger_i \hat{a}^\dagger_j | \psi \rangle \langle \psi | \phi \rangle. \tag{10}
$$

The conventional way of evaluating the force bias proceeds by separately calculating the contribution of each configuration in the CI expansion using the Sherman-Morrison-Woodbury identity, resulting in a cost scaling of $O(N_c N_M + X N M^2)$. Here we present an algorithm with cost scaling as $O(N_c + X M^2)$ by essentially separating the sum over CI excitations from that over Cholesky integral indices in equation [10].

We define the Green’s function matrix for the reference configuration $|\psi_0\rangle$ and the walker configuration $|\phi\rangle$ as

$$
G_j^i = \frac{\langle \psi_0 | \hat{a}^\dagger_{i} \hat{a}^\dagger_{j} | \phi \rangle}{\langle \psi_0 | \phi \rangle} = \left[ \phi(\psi_{0j}^{i\dagger} \phi)^{-1} \psi_{0j} \right]_j, \tag{11}
$$

where $\psi_0$ and $\phi$ are the orbital coefficient matrices of the corresponding configurations, and superscripts and subscripts denote row and column indices, respectively. Note that since we work in the orbital basis of the CI expansion, $\psi_0$ has a particularly simple form with all its columns being unit vectors. Thus the cost of calculating the Green’s function in this basis scales as $O(N^2 M)$. For convenience, we also define the related quantity

$$
\tilde{G}_j^i = -\frac{\langle \psi_0 | \hat{a}^\dagger_{i} \hat{a}^\dagger_{j} | \phi \rangle}{\langle \psi_0 | \phi \rangle} = G_j^i - \delta_j^i. \tag{12}
$$

According to the generalized Wick’s theorem, we have

$$
\langle \psi_0 | \prod_{\mu} \hat{a}^\dagger_{p_{\mu}} \hat{a}^\dagger_{t_{\mu}} | \phi \rangle = \det \left( G_{\{t_{\mu}\}}^{\{p_{\mu}\}} \right), \tag{13}
$$

where the sets of indices $\{p_{\mu}\}$ and $\{t_{\mu}\}$ denote the $k \times k$ slice of the $G$ matrix, $k$ being the rank of the excitation. This expression is obtained by taking pairwise contractions of the operators in the string of excitations according to the generalized Wick’s theorem, with the determinant structure arising due to fermionic permutation parity factors. Therefore, the denominator in equation [10] can be expressed as

$$
\frac{\langle \psi | \phi \rangle}{\langle \psi_0 | \phi \rangle} = \sum_n c_n \det \left( G_{\{t_{\mu}\}}^{\{p_{\mu}\}} \right). \tag{14}
$$

The computational cost scaling of this overlap ratio is thus $O(N_c)$ once the Green’s function has been calculated. Since the Wick’s theorem applies naturally to overlap ratios, we will find it convenient to express matrix elements as ratios with the reference overlap $\langle \psi_0 | \phi \rangle$.

To evaluate the numerator of equation [10] consider the matrix element ratio given by

$$
\frac{\langle \psi_n | \hat{a}^\dagger_{i} \hat{a}^\dagger_{j} | \phi \rangle}{\langle \psi_0 | \phi \rangle} = \frac{\langle \psi_0 \left( \prod_{\mu} \hat{a}^\dagger_{p_{\mu}} \hat{a}^\dagger_{t_{\mu}} \right) \hat{a}^\dagger_{i} \hat{a}^\dagger_{j} | \phi \rangle}{\langle \psi_0 | \phi \rangle}, \tag{15}
$$

where we have dropped the configuration index subscript $(n)$ on the excitations for clarity. This ratio can also be evaluated using the generalized Wick’s theorem and by choosing the appropriate order of operations one can achieve a significant reduction in the cost of calculating the numerator. To this end, we note that the pairwise contractions in the string of excitation operators can be divided into two groups: $i)$ those without any contractions between CI excitations and $\hat{a}^\dagger_{i} \hat{a}^\dagger_{j}$, $ii)$ those containing contractions between two of the CI operators and $\hat{a}^\dagger_{i} \hat{a}^\dagger_{j}$. Algebraically, the two terms are given as

$$
\frac{\langle \psi_0 | \left( \prod_{\mu} \hat{a}^\dagger_{p_{\mu}} \hat{a}_{t_{\mu}} \right) \hat{a}^\dagger_{i} \hat{a}^\dagger_{j} | \phi \rangle}{\langle \psi_0 | \phi \rangle} = \det \left( G_{\{t_{\nu}\}}^{\{p_{\nu}\}} \right) G_{\{t_{\mu}\}} \det \left( G_{\{t_{\nu}\}}^{\{p_{\nu}\}} \right)
$$

$$
= G_{\{t_{\mu}\}}^{\{p_{\mu}\}} \det \left( G_{\{t_{\nu}\}}^{\{p_{\nu}\}} \right) + \sum_{\nu, \lambda} (-1)^{1+\nu+\lambda} G_{\{p_{\nu}\}}^{\{t_{\nu}\}} G_{\{t_{\lambda}\}} \det \left( G_{\{t_{\nu}\}}^{\{p_{\nu}\}} \right), \tag{16}
$$

where on the first line the matrix of size $(k + 1) \times (k + 1)$ is written in a block form, and the notation $\{p_{\mu}\}$ $\{t_{\mu}\}$ indicates the set of indices $\{p_{\mu}\}$ excluding $p_{\nu}$. Using this grouping of terms, we get for the numerator in equation [10]

$$
\sum_n \sum_{ij} c_n L_{ij} \langle \psi_n | \hat{a}^\dagger_{i} \hat{a}^\dagger_{j} | \phi \rangle = \sum_n c_n \det \left( G_{\{t_{\mu}\}}^{\{p_{\mu}\}} \right) \left( \sum_{ij} L_{ij} G_{ij} \right) + \sum_{\nu, \lambda} \left( \sum_{ij} L_{ij} G_{ij} \right) \left( \sum_{ij} L_{ij} G_{ij} \right) + \sum_{\nu} \left( \sum_{ij} L_{ij} G_{ij} \right) \left( \sum_{ij} L_{ij} G_{ij} \right), \tag{17}
$$
where

$$I_p^t = \sum_n c_n \sum_{\nu, \lambda} \delta_{p_{n\nu}} \rho_{t_{n\lambda}} \delta (-1)^{1+\nu+\lambda} \text{det} \left( G^{(p_{n\nu})}_{(t_{n\lambda})} \right)$$

(18)

is an intermediate formed by summing over the CI configurations. The two terms in equation 17 are shown as tensor contraction diagrams in Table 1 for the case of doubly excited CI configurations. Note that a selected CI state does not necessarily include all excitations of a given rank, but since it is not well suited for a tensor representation we use all doubly excited configurations in the table. In practice, the sum over CI excitations in Table 1 is only performed over the configurations in the selected CI state. The first term has a cost scaling of $O(N_c + XN^2M^2)$, while the second one using the intermediate has a scaling of $O(N_c + XM^2)$. If the selected CI state is restricted to an active space of size $A$, the overall cost can be reduced to $O(N_c + XNAM + XAM)$.

3.2. Local energy

The calculation of local energy was discussed in detail in reference [27]. Here, we give a brief summary of the algorithm. Consider the two-body part of the local energy (see equation 8), expressed as

$$E_{L}^2 [\phi] = \sum_{n=1}^{\gamma_{ijkl}} \sum_{\mu} c_{\mu} \gamma_{ijkl} \left[ \langle \psi_{n\mu} | \hat{a}_{i} \hat{a}_{j} | \psi_{n\mu} \rangle \right]$$

(19)

The calculation of the overlap ratios in the denominator is described in the last section for the force bias. The matrix element in the numerator for the $n$th configuration is given by using the Wick’s theorem as

$$\frac{\langle \psi_0 | \left( \prod_{\mu} \hat{a}_{p_{\mu}} \hat{a}_{p_{\mu}} \right) \hat{a}_{i} \hat{a}_{j} | \psi_0 \rangle}{\langle \psi_0 | \psi_0 \rangle} = \text{det} \left( G^{(p_{\mu})}_{(t_{\nu})} G^{(p_{\mu})}_{(t_{\nu})} \right)$$

(20)

where we have again dropped the configuration index subscript. Similar to the force bias calculation, the terms in this determinant can be split into two groups based on the kinds of pairwise contractions: those that do not involve cross contractions between CI and Hamiltonian excitation operators and those that involve at least one such cross contraction. The second group containing cross contractions can be further split into two groups depending on whether one or both of the Hamiltonian excitations are cross contracted with CI excitations. The resulting terms are shown as a tensor diagram in Table 1. Again, we have used all double excited CI configurations only for representational convenience. Different orders of performing the tensor contractions lead to different cost scalings, and using the one described in reference [27] leads to a scaling of $O(N_c + XN^2M^2)$. For a selected CI state restricted to an active space of size $A$, this cost is reduced to $O(N_c + XNAM + XN^2M)$. 

4. RESULTS

In this section, we present the results of our ph-AFQMC/HCI calculations and analyze the convergence of the phaseless error for several systems. In particular, we consider the utility of active space trial states for obtaining accurate energy differences and dipole moments. We used PySCF [43] to obtain molecular integrals and to perform all quantum chemistry wave function calculations. The SHCI code Dice was used to obtain the trial states. The code used to perform ph-AFQMC calculations is available in a public repository [45]. Sources of systematic errors in ph-AFQMC calculations, besides the phaseless bias, include Trotter error, population control bias, errors in the Cholesky decomposition of the electron repulsion integrals, matrix exponential Taylor series truncation errors, and bias due to filtering of rare large fluctuations. We used a conservative time step of 0.005 a.u in all ph-AFQMC calculations. For population control, we used the reconfiguration procedure described in reference [17].

4.1. Hydrogen chains

Hydrogen chain systems are convenient for benchmarking due to their simplicity and availability of accurate density matrix renormalization group (DMRG) ground state energies. [43] First, we consider a chain of 50 equidistant Hydrogen atoms with an interatomic distance $d = 1.6$ Bohr in the minimal sto-6g basis. We performed ph-AFQMC/HCI calculations on this system using progressively larger HCI expansion. These trial states were constructed as truncations of the HCI state obtained with $\epsilon_1 = 10^{-4}$ in the canonical RHF basis. Figure 1 shows the convergence of the phaseless error (calculated as a difference to the DMRG energy reported in reference 1) with the number of configurations in the trial state. We see a nearly monotonic decrease in the phaseless error and the error is less than 2 mH for the trial with $10^6$ configurations. The figure also shows the scaling of the cost of the ph-AFQMC calculation against the number of configurations with respect to the cost of a single configuration calculation. Remarkably, the cost factor for up to $10^4$ configurations is less than 10 and increases roughly linearly with the number of configurations thereafter. This observation is consistent with the scaling relations discussed in section 5 with the $O(N_cX)$ factor in the cost.
TABLE 1. Summary of computational cost scaling of force bias and two-body local energy calculations (given the reference Green’s function matrix $G$). SMW refers to overall cost scaling of the algorithm that makes use of the Sherman-Morrison-Woodbury formula as described in reference 37. The last columns shows tensor contraction diagrams for all distinct types of pairwise Wick’s contractions using all doubly excited configurations $\sum c_{ptqu} \hat{a}_p \hat{a}_q \hat{a}_u \hat{a}_t |\psi_0 \rangle$ as an example. Combining all possible contractions of a given type along with the fermionic parity signs (not shown here) leads to the determinant expressions in equations 17 and 20. The same types of terms arise for higher than doubly excited configurations and the adjacent column shows the optimal cost scaling for calculating each type for a general CI trial with $N_c$ configurations.

| Quantity       | SMW                      | This work                                                                 |
|----------------|--------------------------|---------------------------------------------------------------------------|
| Force bias     | $NM(N_c + X)$            | $N_c + XNM$                                                               |
|                | $N_c + XNM$              | $c_{ptqu} L_{ij}^T \frac{\langle \psi_0 | a_p^\dagger a_q^\dagger a_u a_t | \phi \rangle}{\langle \psi_0 | \phi \rangle}$  |
|                | $N_c + XM^2$             | $c_{ptqu} L_{ij}^T \frac{\langle \psi_0 | a_p^\dagger a_q^\dagger a_u a_t^\dagger a_j | \phi \rangle}{\langle \psi_0 | \phi \rangle}$  |
| Local energy   | $N_c XN^2M$              | $N_c + XNM$                                                               |
|                | $N_c + XNM$              | $c_{ptqu} L_{ij}^T L_{kl} \frac{\langle \psi_0 | a_p^\dagger a_q^\dagger a_u a_t a_j | \phi \rangle}{\langle \psi_0 | \phi \rangle}$  |
|                | $N_c + XN^2M$            | $c_{ptqu} L_{ij}^T L_{kl} \frac{\langle \psi_0 | a_p^\dagger a_q^\dagger a_u a_t a_j | \phi \rangle}{\langle \psi_0 | \phi \rangle}$  |
|                | $N_c + XM^2$             | $c_{ptqu} L_{ij}^T L_{kl} \frac{\langle \psi_0 | a_p^\dagger a_q^\dagger a_u a_t a_j | \phi \rangle}{\langle \psi_0 | \phi \rangle}$  |
|                | $N_c + XNM^2$            | $c_{ptqu} L_{ij}^T L_{kl} \frac{\langle \psi_0 | a_p^\dagger a_q^\dagger a_u a_t a_j | \phi \rangle}{\langle \psi_0 | \phi \rangle}$  |
|                | $X(N_c + NM^2)$          | $c_{ptqu} L_{ij}^T L_{kl} \frac{\langle \psi_0 | a_p^\dagger a_q^\dagger a_u a_t a_j | \phi \rangle}{\langle \psi_0 | \phi \rangle}$  |

**Key for notation**

- $N_c$: number of configurations,
- $N$: number of electrons,
- $M$: number of orbitals,
- $X$: number of Cholesky vectors
- $c$: CI coefficients,
- $L$: Cholesky vectors,
- $G$ and $G'$: Green’s functions
- $i, j, k, l$: Hamiltonian indices;
- $p, q, t, u$: CI excitation indices
scaling of local energy evaluation dominating for large HCI expansions. We found changing the value of $\epsilon_1$ or slightly changing the selection criterion for choosing the configurations to only make a difference in ph-AFQMC energies for smaller number of configurations, leading to similar convergence behaviors for longer expansions.

![Figure 1](image1.png)

**FIG. 1.** Convergence of the ph-AFQMC/HCI phaseless energy error and scaling of the cost of computation with increasing number of configurations for H$_{10}$ using the sto-6g basis at $d = 1.6$ Bohr. The phaseless error is calculated with respect to the near-exact DMRG energy, and the cost factor is calculated as the ratio of computational costs with respect to a single configuration calculation.

![Figure 2](image2.png)

**FIG. 2.** ph-AFQMC/HCI phaseless errors for H$_{10}$ using the cc-pVDZ basis set at different bond lengths. The trial states with different number of configurations are constructed by truncating a (10e, 10o) CASSCF wave function in each case. The hollow symbols show ph-AFQMC/UHF phaseless errors. (They are almost zero for $d = 1.6$ Bohr and $d = 2.4$ Bohr.)

We also studied the H$_{10}$ chain in the cc-pVDZ basis at different bond lengths to gauge the performance of active space trial states. We first performed a (10e, 10o) CASSCF (complete active space self consistent field) calculation and generated trial states by truncating the active space wave function. Figure 2 shows the convergence of the phaseless error with the size of the HCI trial. For all three bond lengths, we see a systematic convergence to an almost vanishing error with the active space trial. The shortest bond length near equilibrium converges rapidly, while the stretched bond length requires almost the full active space wave function to reach convergence. The out of active space phaseless error, arising due to not correlating any orbitals outside the active space in the trial state, is tiny in this case and, more importantly, is very similar for all three bond lengths. We also show ph-AFQMC/UHF phaseless errors in the figure for comparison. ph-AFQMC/UHF is known to be very accurate for hydrogen chains except at stretched geometries. At stretched geometries, a CI expansion based on an unrestricted HF reference has been employed in the past as a trial start and could be a handy tool in other problems as well. The algorithms described in this work can be straightforwardly extended to work with UHF-based CI expansions.

### 4.2. Transition metal oxides

A recent study of transition metal oxide molecules reported benchmark ground state energies using various accurate many-body methods. Here, we use ph-AFQMC/HCI to study convergence of the phaseless errors for active space trials in TiO, CrO, MnO, and FeO. The Troullas-Needs pseudopotential and the corresponding dz basis sets were used at equilibrium geometries in reference [21].

![Figure 3](image3.png)

**FIG. 3.** Shows the convergence of phaseless errors with the number of configurations in the trial state at equilibrium geometries used in reference [21]. We first performed CASSCF calculations with active spaces consisting of the metal 3$d$ and 4$d$ orbitals and oxygen 2$p$ orbitals. The HCI trial states were then generated in a space including the CASSCF active orbitals and the core orbitals, including all electrons. $\epsilon_1 = 10^{-5}$ was used for the HCI calculations. Interestingly, for FeO, CrO, and MnO the phaseless error first increases before converging to a fixed value as the number of configurations in the trial is increased. This peculiar behavior highlights the fact that a lower energy trial state does not guarantee a smaller phaseless error. We note that the trends for smaller expansions are dependent on the particular schemes used for choosing the orbital spaces and for truncating the HCI states. But results for a large number of configurations are largely independent of such somewhat subjective choices. For TiO, using more configurations makes little difference to the phaseless error. We also performed ph-AFQMC/UHF calculations for comparison and found the phaseless errors to be 2(1), 5.3(8), -10(1), and 30.6(9) mH for TiO, CrO, MnO, and FeO, respectively.

The residual phaseless errors can be attributed solely to the out of HCI active space correlation. These errors
The phaseless errors are in mH. The trial states were constructed by truncating active space HCl wave functions. Hollow symbols show ph-AFQMC/UHF errors.

Table 2 shows that the converged phaseless errors are almost identical at the three points. We note that it is crucial to converge the phaseless error of the active space trial, and different geometries may require trial states with different numbers of configurations to achieve convergence. This evidence suggests that in large problems, scalability issues of HCl trial states can be mitigated using active spaces.

4.3. Dipole moments

The mixed estimator of an observable \( \hat{O} \) in the ground state is given by

\[
\langle \hat{O} \rangle_{\text{mixed}} = \frac{\langle \psi_T | \hat{O} | \psi_0 \rangle}{\langle \psi_T | \psi_0 \rangle},
\]

where \( | \psi_0 \rangle \) is the ground state. In ph-AFQMC, one has access to an approximate sampling of the ground state, making the calculation of this mixed estimator convenient:

\[
\langle \hat{O} \rangle_{\text{mixed}} \approx \frac{\sum_i w_i O_L(\phi_i)}{\sum_i w_i},
\]

where

\[
O_L(\phi_i) = \frac{\langle \psi_T | \hat{O} | \phi_i \rangle}{\langle \psi_T | \phi_i \rangle}
\]

is the local observable value.

For observables \( \hat{O} \) that do not commute with the system Hamiltonian, the mixed estimator has a systematic bias due to the trial state used to measure the observable. This bias can be reduced by using the extrapolated estimator, often employed in diffusion Monte Carlo, given by

\[
\langle \hat{O} \rangle_{\text{extrapolated}} = 2 \frac{\langle \psi_T | \hat{O} | \psi_0 \rangle - \langle \psi_T | \hat{O} | \psi_T \rangle}{\langle \psi_T | \psi_T \rangle},
\]

where the variational estimator of the trial state is used to correct the mixed estimator. The accuracy of this extrapolation depends critically on the quality of the trial state. Since ph-AFQMC calculations on molecular systems are typically performed using crude single determinant trials, extrapolation is not a viable option, and backpropagation is used to evaluate variational estimators of the sampled state instead.

Here, we study the behavior of the mixed and extrapolated estimators of dipole moments of a few small molecules. Evaluation of the local dipole moment for an HCl trial state is similar to the force bias calculation outlined in section 3.1, since they both involve matrix elements of one-electron operators.

We first look at the exactly solvable problem of NH\(_3\) in the 6-31g basis (geometry in the SI). We fully diagonalize this (10e, 14o) problem and calculate its ground state dipole moment. Mixed and extrapolated ph-AFQMC estimators were evaluated with trial states consisting of an increasing number of leading configurations from the ground state in the RHF canonical orbital basis. Figure 4 shows the convergence of the estimators with the trial state. In this case, we see a systematic convergence of the variational and mixed estimators to the exact value. The extrapolation works reasonably well, with consistently smaller errors than the mixed estimator.

Table 3 shows the calculated dipole moments for three molecules at equilibrium geometries in the aug-cc-pVQZ

| d | ph-AFQMC/HCl | SHCI | Phaseless error |
|---|--------------|------|-----------------|
| 2.65 | -102.4993(5) | -102.5040(5) | 4.6(7) |
| 3.06 | -102.5531(5) | -102.5584 | 5.3(5) |
| 3.59 | -102.5269(7) | -102.5325(5) | 5.6(8) |

FIG. 3. Convergence of ph-AFQMC/HCI phaseless energy errors for four transition metal oxide molecules using the Trail-Needs dz pseudopotential and basis set. SHCI reference energies were used as references for calculating the phaseless errors. The trial states were constructed by truncating active space HCl wave functions. Hollow symbols show ph-AFQMC/UHF errors.
Table 3. Dipole moments (in a.u.) of three molecules using the aug-cc-pVQZ basis set. The reported ph-AFQMC/HCI values are converged with the number of configurations in the 50 orbital active space trial state.

| Molecule | ph-AFQMC/HCI | RHF | MP2 | CCSD | CCSD(T) | Experiment |
|----------|--------------|-----|-----|------|---------|------------|
|          | Mixed        |     |     |      |         |            |
| CO       | 0.070(3)     | -0.104 | 0.108 | 0.024 | 0.048    | 0.048[2]   |
| BF       | 0.356(4)     | 0.333 | 0.377 | 0.314 | 0.325    | -          |
| H$_2$O   | 0.726(2)     | 0.780 | 0.733 | 0.738 | 0.729    | 0.73[5]    |

5. CONCLUSION

In this work, we presented efficient algorithms for using selected CI trial states in ph-AFQMC. We demonstrated their favorable scaling by showing that simulations with long sCI expansions incur little overhead. In our analysis of the convergence of phaseless error in ground-state energies and dipole moments as a function of the number of configurations, we found it to be non-monotonic in some cases, highlighting the importance of using a sufficient number of determinants in these systems. The use of states restricted to moderately sized active spaces yielded excellent results for energy differences and dipole moments. Our numerical experiments suggest that this extrapolated estimator for small number of configurations in the trial is very poor due to the erroneous variational estimates. For more than $10^4$ configurations, while the mixed estimator seems to be converging to a substantially biased dipole moment value, the extrapolation rectifies this bias reasonably well. The extrapolated estimators are in good agreement with the CCSD(T) and experimental values for all three molecules. Evidently, extrapolation effectively corrects the out of active space bias in the mixed estimator for CO and BF.
may be a practical way to tackle larger systems, where the generation and handling of sCI states are challenging. Finally, we showed that the extrapolated estimator for dipole moments is accurate if enough configurations are present in the trial state. If this behavior turns out to be true in general, extrapolated estimators could be a viable alternative to backpropagation for calculating ground state properties.

Our technique can be employed in different ways for studying challenging systems. It can be used to validate the use of simpler and less expensive trial states in ph-AFQMC for large calculations. ph-AFQMC/HCI can be adopted as an accurate solver in embedding schemes for describing the embedded cluster. It would be interesting to study the feasibility of the extrapolated estimator in larger systems and for calculating two-body properties. Lastly, we note that this technique can be utilized in the quantum-classical hybrid AFQMC (QC-AFQMC) in prototypical and practical quantum computations.[50]

DATA AVAILABILITY

The data that support the findings of this study are available in a public repository at [46]

ACKNOWLEDGEMENTS

AM and SS were supported by the National Science Foundation through the grant CHE-1800584. SS was also partly supported through the Sloan research fellowship. JL thanks David Reichman for support and encouragement. All calculations were performed on the Blanca and Summit clusters at CU Boulder.

REFERENCES

1 Kalos, M. H.; Levesque, D.; Verlet, L. Helium at zero temperature with hard-sphere and other forces. Physical Review A 1974, 9, 2178.
2 Ceperley, D.; Chester, G. V.; Kalos, M. H. Monte Carlo simulation of a many-fermion study. Physical Review B 1977, 16, 3081.
3 Ceperley, D. M.; Alder, B. J. Ground state of the electron gas by a stochastic method. Physical review letters 1980, 45, 566.
4 Nightingale, M. P.; Umrigar, C. J. Quantum Monte Carlo methods in physics and chemistry; Springer Science & Business Media, 1998.
5 Foulkes, W.; Mitas, L.; Needs, R.; Rajagopal, G. Quantum Monte Carlo simulations of solids. Reviews of Modern Physics 2001, 73, 33.
6 Booth, G. H.; Grünbeis, A.; Kresse, G.; Alavi, A. Towards an exact description of electronic wavefunctions in real solids. Nature 2013, 493, 365.
7 Becca, F.; Sorella, S. Quantum Monte Carlo approaches for correlated systems; Cambridge University Press, 2017.
8 Zhang, S.; Krakauer, H. Quantum Monte Carlo method using phase-free random walks with Slater determinants. Physical review letters 2003, 90, 136401.
9 Fahy, S.; Hamann, D. Positive-projection Monte Carlo simulation: A new variational approach to strongly interacting fermion systems. Physical review letters 1990, 65, 3437.
10 Zhang, S.; Carlson, J.; Gubernatis, J. E. Constrained path quantum Monte Carlo method for fermion ground states. Physical review letters 1995, 74, 3652.
11 Zhang, S.; Carlson, J.; Gubernatis, J. E. Constrained path Monte Carlo method for fermion ground states. Physical Review B 1997, 55, 7464.
12 Al-Saidi, W.; Zhang, S.; Krakauer, H. Auxiliary-field quantum Monte Carlo calculations of molecular systems with a Gaussian basis. The Journal of chemical physics 2006, 124, 224101.
13 Al-Saidi, W. A.; Zhang, S.; Krakauer, H. Bond breaking with auxiliary-field quantum Monte Carlo. The Journal of chemical physics 2007, 127, 141101.
14 Suewattana, M.; Purwanto, W.; Zhang, S.; Krakauer, H.; Walter, E. J. Phaseless auxiliary-field quantum Monte Carlo calculations with plane waves and pseudopotentials: Applications to atoms and molecules. Physical Review B 2007, 75, 245123.
15 Purwanto, W.; Zhang, S.; Krakauer, H. An auxiliary-field quantum Monte Carlo study of the chromium dimer. J. Chem. Phys. 2015, 142, 064302.
16 Motta, M.; Zhang, S. Ab initio computations of molecular systems by the auxiliary-field quantum Monte Carlo method. Wiley Interdisciplinary Reviews: Computational Molecular Science 2018, 8, e1364.
17 Hao, H.; Shee, J.; Upadhyay, S.; Ataca, C.; Jordan, K. D.; Rubenstein, B. M. Accurate predictions of electron binding energies of dipole-bound anions via quantum Monte Carlo methods. The journal of physical chemistry letters 2018, 9, 6185–6190.
18 Motta, M.; Shee, J.; Zhang, S.; Chan, G. K.-L. Efficient ab initio auxiliary-field quantum Monte Carlo calculations in Gaussian bases via low-rank tensor decomposition. Journal of chemical theory and computation 2019, 15, 3510–3521.
19 Shee, J.; Arthur, E. J.; Zhang, S.; Reichman, D. R.; Friesner, R. A. Singlet–triplet energy gaps of organic biradicals and polycenes with auxiliary-field quantum Monte Carlo. Journal of chemical theory and computation 2019, 15, 4924–4932.
20 Shee, J.; Rudshuyn, B.; Arthur, E. J.; Zhang, S.; Reichman, D. R.; Friesner, R. A. On Achieving High Accuracy in Quantum Chemical Calculations of 3 d Transition Metal-Containing Systems: A Comparison of Auxiliary-Field Quantum Monte Carlo with Coupled Cluster, Density Functional Theory, and Experiment for Diatomic Molecules. Journal of chemical theory and computation 2019, 15, 2346–2358.
21 Williams, K. T.; Yao, Y.; Li, J.; Chen, L.; Shi, H.; Motta, M.; Niu, C.; Ray, U.; Guo, S.; Anderson, R. J., et al. Direct comparison of many-body methods for realistic electronic Hamiltonians. Physical Review X 2020, 10, 011041.
22 Lee, J.; Reichman, D. R. Stochastic resolution-of-the-identity auxiliary-field quantum Monte Carlo: Scaling reduction without overhead. The Journal of Chemical Physics 2020, 153, 044131.
Lee, J.; Malone, F. D.; Morales, M. A. Utilizing essential symmetry breaking in auxiliary-field quantum Monte Carlo: Application to the spin gaps of the C36 fullereene and an iron porphyrin model complex. *Journal of chemical theory and computation* **2020**, *16*, 3019–3027.

Shi, H.; Zhang, S. Some recent developments in auxiliary-field quantum Monte Carlo for real materials. *The Journal of Chemical Physics* **2021**, *154*, 024107.

Loh Jr, E.; Gubernatis, J.; Scalettar, R.; White, S.; Scalapino, D.; Sugar, R. Sign problem in the numerical simulation of many-electron systems. *Physical Review B* **1990**, *41*, 9301.

Troyer, M.; Wiese, U.-J. Computational complexity and fundamental limitations to fermionic quantum Monte Carlo simulations. *Physical review letters* **2005**, *94*, 170201.

Mahajan, A.; Sharma, S. Taming the Sign Problem in Auxiliary-Field Quantum Monte Carlo Using Accurate Wave Functions. *Journal of Chemical Theory and Computation* **2021**, *17*, 4786–4798.

Giner, E.; Schemama, A.; Caffarel, M. Using perturbatively selected configuration interaction in quantum Monte Carlo calculations. *Canadian Journal of Chemistry* **2013**, *91*, 879–885.

Evangelista, F. A. Adaptive multiconfigurational wave functions. *The Journal of Chemical Physics* **2014**, *140*, 124114.

Holmes, A. A.; Tubman, N. M.; Umrigar, C. J. Heat-Bath Configuration Interaction: An Efficient Selected Configuration Interaction Algorithm Inspired by Heat-Bath Sampling. *J. Chem. Theory Comput.* **2016**, *12*, 3674–3680, PMID: 27428771.

Tubman, N. M.; Lee, J.; Takeshita, T. Y.; Head-Gordon, M.; Whaley, K. B. A deterministic alternative to the full configuration interaction quantum Monte Carlo method. *The Journal of chemical physics* **2016**, *145*, 044112.

Filippi, C.; Assaraf, R.; Moroni, S. Simple formalism for efficient derivatives and multi-determinant expansions in quantum Monte Carlo. *The Journal of chemical physics* **2016**, *144*, 194105.

Assaraf, R.; Moroni, S.; Filippi, C. Optimizing the Energy with Quantum Monte Carlo: A Lower Numerical Scaling for Jastrow–Slater Expansions. *J. Chem. Theory Comput.* **2017**, *13*, 5273–5281, PMID: 28873307.

Dash, M.; Moroni, S.; Schemama, A.; Filippi, C. Perturbatively selected configuration-interaction wave functions for efficient geometry optimization in quantum Monte Carlo. *Journal of chemical theory and computation* **2018**, *14*, 4176–4182.

Pineda Flores, S. D.; Neuscamman, E. Excited state specific multi-Slater Jastrow wave functions. *The Journal of Physical Chemistry A* **2019**, *123*, 1487–1497.

Benali, A.; Gasperich, K.; Jordan, K. D.; Applencourt, T.; Luo, Y.; Bennett, M. C.; Krogel, J. T.; Shulenburger, L.; Kent, P. R.; Loos, P.-F., et al. Toward a systematic improvement of the fixed-node approximation in diffusion Monte Carlo for solids—A case study in diamond. *The Journal of Chemical Physics* **2020**, *153*, 184111.

Shee, J.; Arthur, E. J.; Zhang, S.; Reichman, D. R.; Friesner, R. A. Phaseless auxiliary-field quantum Monte Carlo on graphical processing units. *Journal of chemical theory and computation* **2018**, *14*, 4109–4121.

Sharma, S.; Holmes, A. A.; Jeannairet, G.; Alavi, A.; Umrigar, C. J. Semistochastic Heat-Bath Configuration Interaction Method: Selected Configuration Interaction with Semistochastic Perturbation Theory. *J. Chem. Theory Comput.* **2017**, *13*, 1595–1604, PMID: 28263594.

Smith, J. E.; Mussard, B.; Holmes, A. A.; Sharma, S. Cheap and near exact CASSCF with large active spaces. *J. Chem. Theory Comput.* **2017**, *13*, 5468–5478.

Mahajan, A.; Sharma, S. Efficient local energy evaluation for multi-Slater wave functions in orbital space quantum Monte Carlo. *The Journal of Chemical Physics* **2020**, *153*, 194108.

Rom, N.; Charutz, D.; Neuhauser, D. Shifted-contour auxiliary-field Monte Carlo: circumventing the sign difficulty for electronic-structure calculations. *Chemical physics letters* **1997**, *270*, 382–386.

Löwdin, P.-O. Quantum theory of many-particle systems. I. Physical interpretations by means of density matrices, natural spin-orbitals, and convergence problems in the method of configurational interaction. *Physical Review* **1955**, *97*, 1474.

Ballian, R.; Brezin, E. Nonunitary Bogoliubov transformations and extension of Wick’s theorem. *Il Nuovo Cimento B (1965-1970)* **1969**, *64*, 37–55.

Sun, Q.; Berkelbach, T. C.; Blunt, N. S.; Booth, G. H.; Guo, S.; Li, Z.; Liu, J.; McClain, J. D.; Sayfutyarova, E. R.; Sharma, S.; Wouters, S.; Chan, K.-L. G. PySCF: the Python-based simulations of chemistry framework. *WIREs Comput. Mol. Sci.* **2018**, *8*, e1340.

Buonaura, M. C.; Sorella, S. Numerical study of the two-dimensional Heisenberg model using a Green function Monte Carlo technique with a fixed number of walkers. *Physical Review B* **1998**, *57*, 11446.

Motta, M.; Ceperley, D. M.; Chan, G. K.-L.; Gomez, J. A.; Gull, E.; Guo, S.; Jiménez-Hoyos, C. A.; Lan, T. N.; Li, J.; Ma, F., et al. Towards the solution of the many-electron problem in real materials: Equation of state of the hydrogen chain with state-of-the-art many-body methods. *Physical Review X* **2017**, *7*, 031059.

Trail, J. R.; Needs, R. J. Shape and energy consistent pseudopotentials for correlated electron systems. *The Journal of chemical physics* **2017**, *146*, 204107.

Whitlock, P.; Ceperley, D.; Chester, G.; Kalos, M. Properties of liquid and solid He 4. *Physical Review B* **1979**, *19*, 5598.

Ceperley, D. M.; Kalos, M. *Monte Carlo methods in statistical physics*; Springer, 1986; pp 145–194.

Rothstein, S. A. A survey on pure sampling in quantum Monte Carlo methods. *Canadian Journal of Chemistry* **2013**, *91*, 505–510.

Motta, M.; Zhang, S. Computation of ground-state properties in molecular systems: Back-propagation with auxiliary-field quantum Monte Carlo. *Journal of chemical theory and computation* **2017**, *13*, 5367–5378.

Muenter, J. Electric dipole moment of carbon monoxide. *Journal of Molecular Spectroscopy* **1975**, *55*, 490–491.

Lide, D. R. *CRC handbook of chemistry and physics*; CRC press, 2004; Vol. 85.

Huggins, W. J.; O’Gorman, B. A.; Rubin, N. C.; Reichman, D. R.; Babush, R.; Lee, J. Unbiasing Fermionic Quantum Monte Carlo with a Quantum Computer. *arXiv 2021*. 
