Non-Orthogonal Multi-Slater Determinant Expansions in Auxiliary Field Quantum Monte Carlo

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The Auxiliary-Field Quantum Monte Carlo (AFQMC) algorithm is a powerful quantum many-body method that can be used successfully as an alternative to standard quantum chemistry approaches to compute the ground state of many body systems, such as molecules and solids, with high accuracy. In this article we use AFQMC with trial wave-functions built from non-orthogonal multi Slater determinant expansions to study the energetics of molecular systems, including the 55 molecules of the G1 test set and the isomerization path of the [Cu₂O₂]²⁺ molecule. The main goal of this study is to show the ability of non-orthogonal multi Slater determinant expansions to produce high-quality, compact trial wave-functions for quantum Monte Carlo methods. We obtain systematically improvable results as the number of determinants is increased, with high accuracy typically obtained with tens of determinants. Great reduction in the average error and traditional statistical indicators are observed in the total and absorption energies of the molecules in the G1 test set with as few as 10-20 determinants. In the case of the relative energies along the isomerization path of the [Cu₂O₂]²⁺, our results compare favorably with other advanced quantum many-body methods, including DMRG and complete-renormalized CCSD(T). Discrepancies in previous studies for this molecular problem are identified and attributed to the differences in the number of electrons and active spaces considered in such calculations.

Keywords: AFQMC, Atomization energies, Non Orthogonal Determinants

I. INTRODUCTION

Advances in the comprehension and predictive capabilities of electronic properties of matter, from single atoms to condensed matter systems, are a major quest that permeates many scientific and technological fields. Due to the complexity of the fundamental equations of matter at the atomic scale, over the last several decades, computational methods have become a valuable tool in the discovery, characterization and optimization of new materials. First-principles computational methods, those that do not rely on empirical or experimental parameters and attempt a direct solution to the fundamental equations, have been mostly based on density functional theory (DFT) due to its good predictive capability and modest computational cost. Unfortunately, DFT is based on approximations to electronic exchange and correlation which are known to be unreliable in many materials where these effects dominate or are difficult to approximate, so called strongly correlated materials. As computer power increases and numerical algorithms improve, we are quickly approaching a point where the use of accurate quantum many-body approaches for the study of material properties is becoming feasible. Quantum many-body methods are typically orders of magnitude more computationally expensive than DFT, which has prevented their widespread application to bulk materials in the past, but could offer an accurate alternative with applicability even to strongly correlated materials.

Traditional quantum chemistry methods, like Many-Body Perturbation Theory (MBPT), Coupled Cluster (CC) and Configuration Interaction (CI), can offer accurate solutions to the many-electron problem but their computational cost typically scales unfavorably with system size (N⁶–⁷ for CC methods). While their extension to systems with periodic boundary conditions has been slow, implementations in standard computational packages are more common and applications to solids are appearing more frequently in the literature, including calculations based on second-order Møller-Plesser perturbation theory (MP2) and Random Phase Approximation, Coupled Cluster Singles-Doubles (CCSD) among others.

Quantum Monte Carlo (QMC) methods offer an important alternative to traditional quantum chemistry approaches for the study of many-electron problems, with both finite and periodic boundary conditions. They offer a favorable scaling with system size, typically between N³–⁴, offer excellent parallel efficiency, and are capable of treating correlated electron systems with few approximations. Most QMC methods used in the study of realistic materials rely on a trial wave-function to control the notorious sign problem that plagues all fermionic Monte Carlo methods. The trial wave-function not only controls the magnitude of the resulting approximation, but also the sampling efficiency and the magnitude of statistical uncertainties. Hence, accurate and efficient wave-function ansatz are important to the success of QMC methods in their application to realistic problems in physics, chemistry and material sci-
ence. In this article we examine non-orthogonal multi-
Slater determinant (NOMSD) expansions as an accu-
rate and efficient trial wave-function ansatz for QMC
simulations. We test the efficiency and accuracy of
these wave-functions in combination with the Auxiliary-
Field quantum Monte Carlo (AFQMC) method, as im-
plemented in the QMCPACK\textsuperscript{11,13,17} simulation pack-
age. We show how these wave-functions have the ca-
pacity to systematically reduce errors associated with
the phaseless approximation\textsuperscript{15} in AFQMC, employed to
control the sign problem, with highly compact expan-
sions. These wave-functions have been used in the past
to study strongly correlated lattice Hamiltonians with
great success\textsuperscript{16–24}. They have also been recently popu-
larized in connection with symmetry projection in Gen-
eralized Hartree-Fock theories\textsuperscript{24,25}. While we focus on
AFQMC calculation on molecular systems in this article,
similar improvements are expected when NOMSD wave-
functions are employed in other situations and with other
QMC methods. For example, we have recently employed
these wave-function in studies of lattice Hamiltonians\textsuperscript{20}. The
NOMSD wave-function ansatz now extends the ar-
senal of trial wave-functions employed in QMC calcula-
tions, including truncated CI expansions\textsuperscript{26–28}, Anti-
symmetric Geminal Products (AGP)\textsuperscript{29,30}, Paffians\textsuperscript{31–33},
Bardeen-Cooper-Schrieffer (BCS)\textsuperscript{34,35}, among many oth-
ers.

The structure of this paper is as follows: in the section
II we briefly describe the wave function ansatz and its op-
timization method. Section III shows the application
to the approach to the calculation of total and atomization
energies for a subset of molecules of the G1 set. In section
IV we describe the study of the isomerization path of the
|Cu_{2}O_{2}|^{2+} molecule, a scenario where different contribu-
tions to the correlation energy are significant along the
path making the calculation quite challenging even for tradi-
tional methods. Finally, we discuss clear limitations
with this approach and make concluding remarks.

II. NON-ORTHOGONAL MULTI-SLATER
DETERMINANT TRIAL WAVE FUNCTIONS

The trial wave-functions used in this work have the
typical form:

\[ |\Phi\rangle = \sum_{i=1}^{n_{d}} c_{i} |\phi_{i}\rangle, \]

(1)

where \(|\phi_{i}\rangle\) are Slater determinants and \(c_{i}\) are linear vari-
ational parameters. In traditional quantum Monte Carlo
calculations, multi-determinants trial wave-functions of
this form have been produced from truncated Configu-
ration Interaction (CI) calculations\textsuperscript{27}, or more recently
from selected CI calculations\textsuperscript{28} leading to expansions in
orthogonal determinants connected by particle-hole ex-
citations. While these expansions lead to systematically
improvable results with reasonable stability and robust-
ness, the expansions are typically very large requiring
thousands of terms in order to reach high accuracy\textsuperscript{27}. In
this article, we propose the use of non-orthogonal
Slater determinant expansions, where no orthogonali-
ty constraint is imposed between determinants, hence
\(|\phi_{i}\rangle|\phi_{j}\rangle \neq 0\). In fact, each Slater determinant is rep-
resented as an orbital rotation from a given reference,

\[ |\phi_{i}\rangle = e^{\sum_{j=1}^{n} c_{i,j}^{r} x_{i,j}} |\phi_{i+1}\rangle, \]

where \(Z\) is a Unitary matrix.

Trial wave-functions are obtained by a direct mini-
mization of the energy, \(E = \langle \Phi | H | \Phi \rangle / \langle \Phi | \Phi \rangle\), using a
BFGS-like algorithm and analytical energy gradients, see
Jimenez-Hoyos, C., et al.\textsuperscript{37} for the relevant equations.
We use 2 different approaches, the few-determinant
(FED) algorithm\textsuperscript{24,25} and the resonating Hartree-Fock
(ResHF) approach\textsuperscript{19,20,38}. In the FED algorithm, the
Slater determinant expansion is generated iteratively,
adding and optimizing one determinant in each iteration
to an already existing expansion. During each iteration,
determinants \(|\phi_{i}\rangle\) \((i = 1, 2, \ldots, n_{d} - 1)\) obtained from
previous iterations are kept fixed\textsuperscript{24,25} and the energy is
minimized with respect to the orbital rotation matrix of
the new determinant and all linear coefficients. This
process continues until a given number of determinants
is generated. At this point, the linear coefficients are
re-optimized by solving the associated eigenvalue prob-
lem. In the FED theory, symmetry projectors can be
incorporated straightforwardly. The resulting single-
or multi-reference symmetry-projected FED wave functions
have been shown to be quite accurate. However, we will
not focus on symmetry restoration in this work.

In the ResHF approach the energy, \(E\), is minimized
with respect to all variational parameters in the trial
wave-function, including the rotation matrices of all
determinants and all linear coefficients. In this work,
ResHF trial wave-functions are produced using FED gen-
erated trial wave-functions as input. We use the same
BFGS-like direct optimization algorithm used for FED,
but include all parameters simultaneously in the opti-
mization.

The mean-field orbital used in the FED and ResHF
theories could be restricted-HF (RHF), unrestricted-
HF (UHF), or generalized HF (GHF) wave functions.
The three types of state represent different levels of
symmetry-breaking. In this work, we will mainly focus
on using GHF determinants in which all symmetries of
the Hamiltonian are broken except for the total particle
number. However, it is argued that the GHF wave func-
tion contains the most variational freedom (at the mean-
field level)\textsuperscript{39} comparing to the RHF or UHF states. In
the following, we will demonstrate the flexibility of the
symmetry-broken multi-determinant GHF wave function
in QMC calculations through the combined strength of the
FED and ResHF theories.

III. SIMULATION DETAILS

The MOLPRO\textsuperscript{40} software package was used to perform
Hartree-Fock and CCSD(T) calculations. It was also
used to generate all the integral files (matrix elements of the Hamiltonian in the HF basis) necessary for both AFQMC calculations and for the iterative Hartree-Fock method used to generate the NOMSD wave-functions. The phfnol code was used to generate NOMSD wave-functions. CCSDTQ calculations were performed with the AQUARIUS package. All AFQMC calculations employed the phase-less approximation and were performed with the QMCPACK software package. Unless otherwise stated, we employed a time-step of 0.005 hartrees and 576 walkers, both choices leading to systematic errors below XXX mHa. We employed the frozen-core approximation in all the calculations presented in this article, including both AFQMC and Coupled-Cluster calculations. For a detailed analysis of the influence of frozen-core on the total and atomization energies, see Ref. Correlation-consistent atomic basis sets were used and geometries were taken from Ref. for the molecules in the G1 test set and from Ref. for the study of the isomerization path of the copper oxide molecule.

### IV. G1 TEST SET

In this section we study the energies of 55 molecules of the G1 test set to analyze the accuracy and rate of convergence of the AFQMC method when NOMSD trial wave-functions are used. This set has a long history in both quantum chemistry and quantum Monte Carlo communities, often use as a benchmark to test new developments and capabilities. Accurate reference data exists for all molecules in the set, including atomization energies. A large literature exists with careful analysis of the influence and magnitude of the various approximations employed in theoretical calculations, including effects associated with the choice of basis set and approximations to electronic correlation.

#### A. Total Energies

As an illustrative example, Figure shows the percentage of the correlation energy (measured with respect to CCSDTQ), obtained by AFQMC, as a function of the number of determinants in the NOMSD expansion, for the molecules H_2O, O_2, and NaCl. This figure shows several features of the use of NOMSD wave-functions in AFQMC. First notice that, since all 3 molecules possess weakly correlated electronic structures, single determinant calculations already produce reasonable results with errors around ~1%-4%. In all cases the amount of correlation energy approaches systematically 100% as the determinant expansion in increased, even though the convergence can be from above since AFQMC is not a variational method. In the case of H_2O and O_2, less than 10 determinants are needed to obtain 99.5% of the correlation energy, while at least 50 determinants are needed to obtain a comparable accuracy in NaCl. As will be seen below, molecules with a strong ionic character have a much slower convergence rate with respect to the number of determinants. Nonetheless, even though the specific rate of convergence clearly depends on the specific molecule, rapid convergence is observed in all three cases.

![Figure 1](image)

**Figure 1.** Correlation energy convergence of AFQMC calculations using a Non-Orthogonal expansion with the number of determinants, the inset shows the convergence of the trial wave function as well.

| AFQMC N_{det} | Max. neg. | Max. pos. | ME  | MAE  | STDEV |
|----------------|-----------|-----------|-----|------|-------|
| 1 det          | -58.94    | 12.81     | 0.32| 4.02 | 9.84  |
| 5 det          | -1.85     | 5.83      | 0.22| 0.75 | 1.27  |
| 20 det         | -1.11     | 2.57      | 0.01| 0.34 | 0.64  |

In order to have a more quantitative characterization of the accuracy of the AFQMC-NOMSD approach, we
Figure 2. Comparison of AFQMC total energies differences with NOMSD trial wave functions with 1, 5, 20 determinants against Couple Cluster calculations, including single, double, triple and quadruple excitations. The red arrows indicate that the values of that difference are greater than 5 mHa and point to its explicit value performed CCSDTQ calculations for a subset of the 55 molecules considered in this work using Dunning's cc-pVDZ basis set. We were forced to limit our analysis to a subset of the 42 molecules in the test set due to difficulties with the convergence of CCSDTQ for some of the molecules. We expect CCSDTQ to provide reliable results for these molecules, with errors below 1 mHa. Figure 2 shows the error in the total energy calculated by AFQMC-NOMSD when measured with respect to CCSDTQ. We present results using 1, 5, and 20 determinants in the NOMSD expansions to show the convergence of the correlation energy as the expansion is increased. Table IV A shows the associated performance statistics for the energy differences. For the selected set of molecules, the mean absolute error decreases from 4.02 mHa to 0.75 mHa by going from single determinant to a 5 determinant expansion, with a further reduction to 0.34 mHa when the expansion is increased to 20 determinants. In general, all statistical measures of the energy difference show a significant and systematic reduction between single determinant calculations and NOMSD with increasingly larger expansion sizes. Notice that the choice of a 20 determinant expansion is somewhat arbitrary, with the intention of showing a very significant reduction on the errors with just a handful of determinants. While the magnitude of the errors is dependent on the molecule, the capacity for significant improvement with a very compact expansion is universally observed.

B. Atomization Energies

Figure 3 shows the error in the atomization energy, calculated with AFQMC-NOMSD, for the 55 molecules considered in this work. Table II shows the associated performance statistics. Reference values have been obtained from Feller et al. by subtracting the Zero Point Energy (ZPE), Spin Orbit (SO), Core Valence (CV), Scalar Relativistic (SR) and the Diagonal Born-Oppenheimer Correction (DBOC) contributions from the experimental values. Atomization energies have been extrapolated to the Complete Basis Set (CBS) limit using results with Dunning’s cc-pV(X)Z basis sets, with X = {D, T, Q}. We used the mixed Gaussian/Exponential formula, \( E(n) = E_{CBS} + A e^{-(n-1)} + B e^{-(n-1)^2} \), which has been shown to perform well for CCSD(T). Similar to the previous section, we show results for expansions of size 1, 5, and 20, with the goal of showing the capacity of this approach for error reduction with short, compact expansions.

Table II. Raw performance statistics of the AFQMC atomization energies error with the NOMSD expansion respect to the reference values. All quantities are in mHa.

| AFQMC N_{det} | Max. neg. | Max. pos. | ME | MAE | STDEV |
|---------------|-----------|-----------|-----|-----|-------|
| 1 det         | -46.23    | 21.05     | 5.42| 7.43| 8.71  |
| 5 det         | -4.14     | 9.61      | 2.05| 2.71| 2.77  |
| 20 det        | -5.23     | 6.18      | 0.14| 1.22| 1.77  |

As expected from the discussion above, the NOMSD expansion is able to reduce significantly the errors of
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Figure 3. Atomization Energies for the set of molecules, comparison of the extrapolated data of AFQMC for the cc-pVXZ, $X = \{D, T, Q\}$, displaying the Mean absolute error in comparison to the reference values.

AFQMC throughout the test set. Overall, the mean absolute error is reduced from 7.43 mHa to 2.71 mHa when going from a single determinant to a 5 determinant expansion, and to 1.22 mHa when 20 determinants are used. Several observations can be made upon careful inspection of the various molecules in the set. First, we notice that for many molecules a 5 determinant expansion is enough to drastically reduce the error in the atomization energies, often with error reductions of over 90%. We can also notice a set of molecules for which convergence is slow, including for example LiF and NaCl. These molecules have a strong ionic character that seems to lead to slow convergence with respect to expansion length. We must point out that the errors in the atomization energies discussed above contain, in addition to any bias associated with the AFQMC method, a potentially significant contribution from basis set extrapolation since the largest basis set we considered was cc-pVQZ. In the case of molecules containing S and Si, we believe that inaccuracies in the basis set extrapolation account for a significant fraction of the resulting errors on the atomization energies since total energy calculations agree very well with CCSDTQ calculations.

V. COPPER OXIDE ISOMERIZATION PATH

The study of the isomerization path of the $[Cu_2O_2]^{2+}$ molecule has become a common practice in the last decade to test the capacity of ab-initio and quantum chemistry methods to accurately describe the energetics of correlated molecular problems. As pointed out by K. Samanta et al., the interest comes from the dissimilar nature of the correlation energy in the molecule through the path. A successful description of the relative energy of the molecule along the path requires methods that offer a balanced treatment of both static and dynamic components of the correlation energy, since both terms have dominant contributions at different points along the path. Figure 4 shows a schematic representation of the stable isomers at the endpoints the isomerization path. We use the same geometry, pseudopotential and basis set employed in several previous studies of this molecule in order to be able to draw a direct comparison with other correlated electronic structure approaches. For a detailed description of the geometry, pseudopotential, basis set and summary from previous theoretical calculations, we refer the reader to Refs. and references therein.

Previous studies of this molecule using advanced electronic structure methods including Density Matrix Renormalization Group (DMRG) Complete Renor-
ormalized Coupled Cluster (CR-CC)\textsuperscript{53} and Projected Hartree-Fock (PHF)\textsuperscript{44} appear to lead to discrepancies on the relative energy differences across the isomerization path. In particular, PHF calculations reported in Ref.\textsuperscript{44} seem to lead to larger energy differences when compared to DMRG and CR-CC. As shown below, these discrepancies seem to be related to the different choices of core and active spaces selected in each of the calculations. While all these calculations appear to used the same atomic basis set and the same molecular geometries, DMRG calculations reported in Ref.\textsuperscript{52} used an active space of \((28e,32o)\) leading a calculation with 28 correlated electrons, CR-CC calculations correlated explicitly the 2s and 2p orbitals of oxygen in addition to the 4s and 3d orbitals of Cu leading to 32 correlated electrons, while PHF calculations in Ref.\textsuperscript{44} correlated all 52 electrons in the calculation. As will be shown, the resulting differences in the number of core electrons in each of the calculations leads to the observed discrepancies in previous results, rather than strong inaccuracies in the predicted relative energies.

Figure 5. Convergence of the AFQMC-NOMSD total energy for the \([\text{Cu}_2\text{O}_2]^{2+}\) molecule as a function of the number of determinants in the expansion for the endpoints of the isomerization path.

Figure 5 shows the dependence of the AFQMC-NOMSD total energy with the number of terms in the expansion for the 2 endpoints of the isomerization path. The total energy of configuration A converges quickly, requiring only 75 determinants for an accuracy of 1 kcal/mol, since in this case dynamic correlation is dominant and is efficiently captured by the AFQMC method. Even in this complicated scenario, NOMSD offers a systematically convergent, compact choice for trial wave-function.

VI. DISCUSSION

Several observations about the NOMSD approach are appropriate at this point. First we must point out that, similar to truncated CI expansions, the NOMSD expansion is not size extensive nor size consistent. This means that the number of terms in the expansion necessary for an equivalent description of the system will ultimately scale exponentially as a function of the sys-
tem size. While this creates serious problems for direct use of truncated CI (or non-orthogonal) expansions in quantum chemistry methods for periodic systems, the relevant question in our case is not whether the wave-function is size-consistent but whether the reduction of the phase-less error is. While a study of the scaling of the phase-less error with expansion length is outside the scope of the work presented in this article, it is unlikely that in the thermodynamic limit non-exponential behavior is obtained. Nonetheless, for systems of typical interest (up to 100 atoms), this approach leads to a simple and well-defined path for error reduction. For larger calculations, it is possible to employ the NOMSD approach in an active space approach, where only a small subset of the orbitals are included in the construction of the correlated trial wave-function. This will lead to better scaling and higher efficiency without sacrificing too much accuracy. A future publication will discuss modifications and improvements of the method needed in its application to correlated materials in periodic boundary conditions.

Another important consideration is the evaluation efficiency of the NOMSD wave-function compared to traditional expansions based on truncated or selected CI. Since different configurations in orthogonal expansions differ by a finite number of orbitals, fast low-rank update schemes can be used[28] which leads to highly efficient evaluation routines. In the case of NOMSD expansions, no such optimizations have been devised leading to much higher evaluation cost as a function of expansion length. A proper comparison of the two methods requires a careful analysis of implementation details, which is outside the scope of this work. Nonetheless, we believe that the current approach offers sufficiently compact expansions to compensate for the lower evaluation efficiency. A detailed analysis of the computational aspects of the method will be presented in a separate publication.

VII. CONCLUSIONS

The AFQMC method offers a powerful alternative for the study of quantum many-body problems in physics, chemistry and material science. Its ability to handle both weakly and strongly correlated electronic structure problems with favorable scaling offers an excellent alternative to traditional methods in quantum chemistry and ab-initio electronic structure. When combined with flexible and efficient trial wave-functions, the method has the potential to become the method of choice for the study of realistic quantum systems. In this article, we present non-orthogonal Multi-Slater determinant expansions as an accurate and compact choice for trial wave-functions in AFQMC. They offer the flexibility, simplicity and compact representation needed for realistic calculations of materials and complicated molecular systems. NOMSD expansions have the capability to recover significant fractions of the correlation energy with a modest number of terms, compared to traditional orthogonal expansions based on configuration interaction which typically have slowly decaying tails which require orders of magnitude more terms for similar accuracy.

For weakly correlated systems, including the molecules in the G1 test set, we showed the capacity of the NOMSD approach to systematically reduce the errors in total and atomization energies with short expansions, even as small as 5 determinants in many cases. We obtain a mean absolute error of 1.22 mHa in the atomization energies of the 55 molecules considered in this work with a 20 determinant expansion, which includes potential errors associated with basis set extrapolation. In addition, we obtain an mean absolute error of 0.34 mHa in the total energies when comparing against CCSDTQ$_0$ for a subset of the 55 molecules in the cc-pVDZ basis. These errors can easily be reduced further with longer expansions if desired.

For the correlated molecular system, [Cu$_2$O$_2$]$^{2+}$, we showed the vast improvement obtained in the relative energies along the isomerization path from the use of NOMSD expansions in combination with AFQMC. In this case, single determinant trial wave-functions lead to large errors in the relative energies along the path, with errors as large as 30 kcal/mol when compared to advanced electronic structure methods like DMRG and CR-CC. In this case, expansions of several hundred determinants were necessary to obtain well converged results. We also showed that discrepancies in previous calculations can be well explained by the differences in the number of core electrons used, obtaining excellent agreement with CR-CC and DMRG when consistent choices are made. We believe that the work presented in this article will lead to a further examination and optimization of the use of non-orthogonal compact expansions in quantum Monte Carlo and will further contribute to the quest for accurate and efficient wave-function ansatz for correlated quantum many-body systems.

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