Multireference configuration interaction and perturbation theory without reduced density matrices

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The computationally expensive evaluation and storage of high-rank reduced density matrices (RDMs) has been the bottleneck in the calculation of dynamic correlation for multireference wave functions in large active spaces. We present a stochastic formulation of multireference configuration interaction (MRCI) and perturbation theory (MRPT) that avoids the need for these expensive RDMs. The algorithm presented here is flexible enough to incorporate a wide variety of active space reference wave functions, including selected configuration interaction, matrix product states, and symmetry-projected Jastrow mean field wave functions. It enjoys the usual attractive features of Monte Carlo methods, such as embarrassing parallelizability and low memory costs. We find that the stochastic algorithm is already competitive with the deterministic algorithm for small active spaces, containing as few as 14 orbitals. We illustrate the utility of our stochastic formulation using benchmark applications.

1. INTRODUCTION

A quantitative treatment of electronic structure in molecules with strong electron interactions has been a challenge for quantum chemical methods. It is often useful to distinguish between two flavors of electron correlation: static and dynamic. Static correlation is a result of nearly degenerate electronic states and strong interactions between them. A telltale sign of this type of correlation is the dramatic failure of single-reference methods like Hartree-Fock (HF) accompanied by divergences in Møller-Plesset perturbation theory and coupled cluster theory. Multireference (MR) methods overcome this shortcoming by treating all (or a large number of) configurations in an active space on an equal footing. The active space usually consists of chemically relevant nearly degenerate valence orbitals. Examples of MR methods include full configuration interaction (FCI), density matrix renormalization group (DMRG),17 semistochastic heat bath configuration interaction (SHCI)18 full configuration interaction quantum Monte Carlo (FCIQMC)19,20 and their self consistent field extensions, known as complete active space self consistent field (CASSCF).21,22 DMRG-SCF17,23 SHCI-SCF24 and FCIQMC-SCF25,26 respectively. While CASSCF is limited to rather small active spaces (usually less than 20 electrons and orbitals), the rest of these methods have been used in considerably larger active spaces.27–29

Dynamic correlation is related to the fact that the usual Gaussian orbitals are inefficient at describing the Coulomb hole of an electron, which results in an extremely slow convergence of the correlation energy with the number of basis functions. To overcome this difficulty, both reasonably large basis sets (usually triple zeta basis) and explicitly correlated terms, which are functions of the inter-electronic distance, are needed to obtain chemical accuracy. The difficulty of having to use large orbital spaces is somewhat mitigated by the fact it is sufficient to use wave functions that explicitly contain only single or double excitations. MR methods suitable for capturing dynamic correlations include perturbation theory (e.g. complete active space second order perturbation (CASPT2) theory30–32 and n-electron valence perturbation (NEVPT) theory33–35) configuration interaction (e.g. multireference configuration interaction (MRCI) approaches36–38), multireference coupled cluster theories (MRCC),39 canonical transformation (CT) theory40,41 or the driven similarity renormalization group (DSRG) method42–44

Efficient implementations of all flavors of multireference theories that are used to capture dynamic correlations utilize internally contracted states (we will describe them in more detail in Section 2.1). The great advantage of using internally contracted states is that the cost of the calculation no longer scales exponentially with the size of the active space, however, the disadvantage is that the memory cost of the calculation is a high order polynomial of the active space size. For example, in perturbation theory and configuration interaction interaction theory, up to fourth-order reduced density matrices in the active space are needed. The cost of storing these reduced density matrices scales as the $8^{n}$ power of the number of orbitals in the active space. Although this is still manageable for small active spaces containing 20 or fewer orbitals (the limit of a CASSCF calculation), it becomes prohibitive for the large active space calculations of the type that can be performed using modern MR methods such as DMRG, FCIQMC and selected CI45–47. Various approaches and approximations have been proposed in the past, including (a) the use of cumulant approximation48,49 (b) storing 4-RDM as batches of transition 3-RDM on disk,50 (c) uncontracting terms that require 4-RDMs (partial contraction),51,52 (d) treating some terms that require 4-RDMs using matrix product states,53–55 (e) performing time-propagation.56 Each of these approaches have shortcomings, for example, the cumulant approximation is highly unstable and leads to significant intruder state problems that can sometimes be fixed by including
a level shift. Although the approaches (b) and (c) reduce the memory cost, they still require one to generate and store the 3-RDM which is quite expensive. The apparent exponential scaling of the uncontracted terms in (c) can be avoided using matrix product states perturbation theory.

Finally, the time-dependent approach completely eliminates the need to store RDMs, but so far it has only been demonstrated to work with NEVPT2, where the special structure of the zeroth-order Dyall’s Hamiltonian is used and it remains to be seen if this approach can be extended to more general perturbation theories and configuration interaction.

In this article, we present a stochastic formulation of the MRCI and NEVPT2 methods, that eliminates the need for constructing and storing the reduced density matrices. To reduce the number of parameters, we use a higher level of contraction, than the internal contraction, called strong contraction (SC)

We use an algorithm that is essentially identical to the Variational Monte Carlo (VMC) to optimize the wave function and calculate the energies of the SC-MRCI, and we term this approach SC-MRCI(s). This algorithm is extended to sample the Davidson size-consistency correction allowing us to calculate the SC-MRCI+$Q$ energy up to small stochastic noise. For SC-NEVPT2(s), we again use the stochastic method to calculate the norms and energies of the perturbet states, which allows us to calculate the first-order wave function and second-order energy corrections. The approach here is agnostic to the type of wave function used for performing the active space calculation and is compatible with FCI, selected CI, matrix product states, and symmetry-projected Jastrow mean field states.

The rest of this article is organized as follows: First, we briefly review the wave functions arising from the various contraction schemes and follow with the presentation of the SC-MRCI(s) and SC-NEVPT(s) algorithms. We also report details of our implementation when the FCI or selected CI methods are used to obtain the reference state. Finally, we report benchmark calculations performed using these methods, along with comparisons with the deterministic MRCI and NEVPT2 algorithms.

2. THEORY

2.1. Overview of contraction schemes

The zeroth-order wave function $|\phi_0\rangle$ is assumed to be an accurate representation of the exact wave function in the active space. It can be obtained by one of the several methods listed in the introduction, although in this work we will only be using CASSCF. Next, we begin by looking at various contraction schemes used in multireference theories to calculate dynamical correlation.

In the uncontracted methods, the wave function spans the entire first-order interacting space (FOIS) which consists of all singly and doubly excited determinants that couple to the active space reference through the Hamiltonian (our description is different than one in which FOIS is described as the space spanned by internally contracted states). It is only possible to use the uncontracted scheme with relatively small systems (and active spaces). Various contraction schemes have been proposed to tackle larger systems. In the fully internally contracted (FIC) approach, single and double excitation operators are directly applied to $|\phi_0\rangle$ instead of individual determinants, resulting in a more compact wave function given by

$$\psi_{\text{FIC}} = c_0|\phi_0\rangle + \sum_{p,a} c_p^a a_p^\dagger a_p|\phi_0\rangle + \sum_{p,q} c_p^q a_p^\dagger a_q|\phi_0\rangle + \sum_{p,q,r,a} c_p^q a_p^\dagger a_r^\dagger a_q|\phi_0\rangle + \sum_{p,q,r,s} c_p^q r_s a_p^\dagger a_q^\dagger a_r^\dagger a_s|\phi_0\rangle,$$

where $a, b, \ldots$ denote virtual orbitals, while $p, q, \ldots$ denote internal (core and active) ones. Notice that the number of parameters in the FIC scheme is at most quartic in the size of the active space, unlike the uncontracted scheme, where it is exponential. Despite the enormous reduction in the number of parameters, the FIC results are usually in very good agreement with those of the uncontracted methods. One of the drawbacks of the FIC scheme relative to the uncontracted wave function is that the internally contracted states ($a_p^\dagger a_q^\dagger a_p^\dagger a_q^\dagger|\phi_0\rangle$) are no longer orthogonal, which often leads to ill-conditioned generalized eigenvalue problems. In most algorithms, this difficulty is overcome by explicitly diagonalizing the overlap matrix and eliminating the zero-eigenvectors. The IC approximation also requires construction of up to rank five RDMs which becomes very expensive as the size of the active space increases. One of the ways of avoiding this is to uncontract certain classes of excitations leading to a partially contracted (PC) scheme. This has been employed in Werner’s group in the development of Werner-Knowles (WK) and later the improved Celani-Werner (CW) MRCI.

It performs very well for smaller active spaces but has an exponential bottleneck.

The strong contraction (SC) approximation alleviates the non-orthogonality problem by further contracting the subspaces through Hamiltonian matrix elements. Here, we follow the notation introduced by Malrieu et al. Let $S_l^{(k)}$ denote the subspace of FIC-FOIS, where $k$ is the change in the number of active electrons ($-2 \leq k \leq 2$) and $l$ denotes the configuration of electrons in the core and virtual spaces. In the SC theory, only a single state $|\psi_l^{(k)}\rangle$ from each $S_l^{(k)}$ is used. Specifically,

$$|\psi_l^{(k)}\rangle = P_l^{(k)}H|\phi_0\rangle,$$

where $P_l^{(k)}$ is the projector onto the $S_l^{(k)}$ space. Equivalently, this state is obtained by eliminating the active
indices of the FIC states by contracting with the one and two electron integrals. For example, the following state from the $S_{ab}^{(-2)}$ subspace is used:

$$|\psi_{ab}^{(-2)}\rangle = \sum_{pq} ((ab|pq) - (ab|qp)) a^p_0 a^q_0 a^p a^q |\phi_0\rangle. \quad (3)$$

An exception to this rule is made for the $S_{0}^{(0)}$ space, which is represented by the state $|\phi_0\rangle$. Implicit in this simplification is the assumption that $|\phi_0\rangle$ is the eigenstate of the active space Hamiltonian ($H_0$), otherwise an additional term $H_0|\phi_0\rangle$ should also be included. Using these states the SC wave function is described as

$$|\psi_{SC}\rangle = \sum_{k,l} c^{(k)}_l |\psi_l^{(k)}\rangle.$$ 

Note that the states $|\psi_l^{(k)}\rangle$ are mutually orthogonal (although not normalized).

Neese et al. have argued that using the SC approximation does not lead to a large gain in efficiency in the deterministic MRCI algorithm.\cite{Neese2002} In our stochastic formulation, we found the SC approximation to lead to a much easier optimization problem. It is also known to help avoid the intruder state problems in perturbation theory. Thus we will focus on the SC methods below. It is worth mentioning that an alternative scheme called the external contraction was proposed by Siegbahn, which effectively eliminates the virtual orbitals from the calculation. However, it scales exponentially with the size of the active space and in its current form is only applicable when the active space wave function is expressed as a linear combination of determinants.\cite{Siegbahn1995}

### 2.2. SC-MRCI(s)

In this section, we outline the use of the SC-MRCI wave function as a VMC ansatz and its optimization using our improved orbital space VMC algorithm. In VMC, the energy of a wave function $|\psi(p)\rangle$, where $p$ is the set of parameters, can be computed using importance sampling as

$$\frac{\langle \psi(p)|H|\psi(p)\rangle}{\langle \psi(p)|\psi(p)\rangle} = \sum_n \frac{|\langle n|\psi(p)\rangle|^2}{\langle \psi(p)|\psi(p)\rangle} \frac{\langle n|H|\psi(p)\rangle}{\langle n|\psi(p)\rangle} \rho_n,$$ 

where $|n\rangle$ is a Slater determinant walker, $\rho_n = |\langle n|\psi(p)\rangle|^2$ is the probability distribution used for Monte Carlo sampling. The quantity sampled is called local energy, given by

$$E_L[n] = \frac{\langle n|H|\psi(p)\rangle}{\langle n|\psi(p)\rangle} = \sum_n \frac{\langle n|H|n\rangle}{\langle n|\psi(p)\rangle} \frac{\langle m|\psi(p)\rangle}{\langle n|\psi(p)\rangle}.$$ 

For an efficient calculation of local energy, it is essential to be able to calculate the walker overlap ratios $\frac{\langle n|\psi(p)\rangle}{\langle n|\psi(p)\rangle}$ appearing in the above equations cheaply.

We now consider these overlaps carefully for the SC-MRCI wave function. Note that each walker belongs to a unique $S_{0}^{(k)}$ subspace. We will denote the subspace a walker $|n\rangle$ belongs to by $S_{0}^{(k)}$. Thus the overlap of the walker with a general contracted state is given by

$$\langle n|\psi_l^{(k)}\rangle = \begin{cases} \delta_{k,0}\delta_{l,0} \langle n|\phi_0\rangle, & \text{if } |n\rangle \in S_{0}^{(0)}, \\ \delta_{k,k_l}\delta_{l,l_n} \langle n|H|\phi_0\rangle, & \text{if } |n\rangle \notin S_{0}^{(0)}. \end{cases}$$ 

The overlap of the walker with $|\psi_{SC}\rangle$ is given by

$$\langle n|\psi_{SC}\rangle = c^{(k_n)}_n \langle n|\psi_l^{(k_n)}\rangle.$$ 

As $|\phi_0\rangle$ is assumed to be a selected CI wave function, its overlap with a walker can be calculated in an average $O(1)$ time by storing the determinants and coefficients in a hash table. We note that the local energy calculation is feasible for any wave function that allows efficient evaluation of these overlaps.

The walkers are sampled from the probability distribution $\rho_n$ by using the rejection free continuous time Monte Carlo (CTMC) algorithm,\cite{CM2016, MS2017} the details of which can be seen in Ref.\cite{CM2016} All quantities required for CTMC sampling are calculated and stored during the local energy evaluation at no additional cost.

We now turn to the problem of optimizing the wave function parameters, which in this case are the CI coefficients. At first glance, it would appear that analogous to the deterministic algorithms, the linear method\cite{CM2016, MS2017} should be able to optimize this linearly parametrized wave function in a single step. While this is true in theory, the linear method becomes very expensive for a large number of parameters both in terms of time and memory cost.\cite{CM2016, MS2017} In our experiments, we have found that it can only be feasibly applied when the number of coefficients is less than about 50,000. Since the number of states in an MRCI wave function often exceeds this number, the linear method does not appear to be a suitable choice in this problem. We instead choose AMS-Grad, an accelerated stochastic gradient method developed in the machine learning community.\cite{AMSGrad} Its utility in wave function optimization in VMC has recently been reported.\cite{CML2018, CM2019, MS2017} It should be noted that SGD has been used implicitly to solve CI problems in FCIQMC and its many variants.\cite{AMSGrad} AMSGrad requires an estimate of the energy gradient, which can be sampled as

$$g_i = \frac{\partial E}{\partial p_i} = \langle \psi_i(p)|n\rangle \left(\frac{\langle \psi_i(p)|n\rangle}{\langle \psi(p)|n\rangle} (E_L[n] - E)\right)_{\rho_n},$$ 

where $\psi_i(p) = \left| \frac{\partial \psi (p)}{\partial p_i} \right|$ is the wave function derivative and $E$ is the energy of the wave function. For $|\psi_{SC}\rangle$, the wave function derivative overlaps are given by

$$\langle n|\psi_{k,l}\rangle = \delta_{k,k_n}\delta_{l,l_n} \langle n|\psi_l^{(k_n)}\rangle,$$ 

where $\delta_{k,k_n}\delta_{l,l_n}$ is the overlap between the walker with a general contracted state.
where \( |\psi_{k,l}\rangle \) denotes the derivative with respect to \( c_l^{(k)} \). These quantities are needed for local energy calculation (Equation 6) and are thus easily obtained.

The Davidson size-consistency correction is given by

\[
\Delta_D E = (1 - a_0^2)(E_{\text{SC-MRCI}} - E_0^{(0)}),
\]

where \( a_0 \) is the coefficient of the normalized reference in the normalized SC-MRCI wave function. \( a_0 \) is not entirely trivial to obtain because we do not explicitly know the norm of each of the SC states. Instead, we calculate \( a_0^2 \) by first noting that

\[
a_0^2 = \frac{\langle \phi_0 | \psi_{\text{opt}} \rangle^2}{\langle \phi_0 | \phi_0 \rangle \langle \psi_{\text{opt}} | \psi_{\text{opt}} \rangle} = \left( c_0^{(0)} \right)^2 \frac{\langle \phi_0 | \phi_0 \rangle}{\langle \psi_{\text{opt}} | \psi_{\text{opt}} \rangle},
\]

where \( |\psi_{\text{opt}}\rangle \) is the optimized SC-MRCI wave function and \( c_0^{(0)} \) is the (known) coefficient of \( |\phi_0\rangle \) in this wave function. This can be sampled using the CTMC algorithm as

\[
\left( c_0^{(0)} \right)^2 \frac{\langle \phi_0 | \phi_0 \rangle}{\langle \psi_{\text{opt}} | \psi_{\text{opt}} \rangle} = \sum_n \left| \langle n | \psi_{\text{opt}} \rangle \right|^2 \langle \psi_{\text{opt}} | \psi_{\text{opt}} \rangle \left( c_0^{(0)} \right)^2 \frac{\left| \langle n | \phi_0 \rangle \right|^2}{\left| \langle n | \psi_{\text{opt}} \rangle \right|^2} = \langle \delta_{n,0} \delta_{n,0} \rangle_{\rho_0}.
\]

2.3. SC-NEVPT2(s)

The SC-NEVPT first-order correction is given by

\[
|\psi^{(1)}\rangle = \sum_{k,l \neq 0} \frac{1}{E_0^{(0)} - E_l^{(k)}} |\psi_l^{(k)}\rangle,
\]

where, the perturber state energies \( E_l^{(k)} \) are defined as

\[
E_l^{(k)} = \frac{\langle \psi_l^{(k)} | H_D | \psi_l^{(k)} \rangle}{\langle \psi_l^{(k)} | \psi_l^{(k)} \rangle},
\]

And the second order SC-NEVPT energy correction is given by

\[
E^{(2)} = \sum_{k,l \neq 0} \frac{1}{E_0^{(0)} - E_l^{(k)}} \frac{\langle \psi_l^{(k)} | \psi_l^{(k)} \rangle}{\langle \psi_l^{(k)} | \psi_l^{(k)} \rangle},
\]

In Eq. 14 \( H_D \) is Dyall’s Hamiltonian,\(^{12}\) the zeroth-order Hamiltonian employed in NEVPT. It is defined as

\[
H_D = \sum_i \epsilon_i a_i^\dagger a_i + \sum_a \epsilon_a a_a^\dagger a_a + H_0,
\]

where \( i \) and \( a \) denote the orbitals obtained by diagonalizing the core and virtual generalized Fock operators, respectively, and \( \epsilon_i \) and \( \epsilon_a \) the corresponding eigenvalues. \( H_0 \) is the full core-averaged Hamiltonian in the active space.

The energies \( E_l^{(k)} \) can be obtained using Monte Carlo sampling of the numerator and denominator separately

\[
\frac{\langle \psi_l^{(k)} | H_D | \psi_l^{(k)} \rangle}{\langle \psi_l^{(k)} | \psi_l^{(k)} \rangle} = \sum_n \frac{\langle n | \psi_l^{(k)} \rangle^2}{\langle n | \psi_l^{(k)} \rangle} \langle n | H_D | n \rangle \frac{\langle n | \psi^{(k)} \rangle}{\langle n | \psi^{(k)} \rangle},
\]

where \( |\psi_s\rangle \) wave function is used for importance sampling. In our calculations, we use the sampling wave function given by

\[
|\psi_s\rangle = \sum_{k,l} c_l^{(k)} |\psi_l^{(k)}\rangle,
\]

where we choose the coefficients \( c_l^{(k)} \) randomly, with the condition that \( c_0^{(0)} \) is about an order of magnitude bigger than other coefficients. In principle, it is sufficient to choose any state \( |\psi_s\rangle \) that has a non-zero overlap with all the perturber states \( |\psi_l^{(k)}\rangle \). The quantities in Eq. 16 for all classes \( S^{(k)} \) are sampled together using a single CTMC run similar to the one used for SC-MRCI(s) calculations. Note that the square norm ratios required for calculating the second-order energy correction (cf. Eq. 15) are also obtained in the same sampling run. In our experience, calculating the energy correction requires more sampling effort than calculating the coefficients in the wave function correction, likely because the variance of the quantities sampled to estimate the norms of the SC states is higher. Some perturber states have a small norm, which can be of the same order as the stochastic noise. This can cause numerical instabilities because the norms appear in the denominator of Eq. 14. To avoid this, the perturber states with a small norm are screened out. The screening does not cause significant error in the SC-NEVPT2 energies because the norm appears in the numerator of Eq. 15.

2.4. Implementation

We have implemented these algorithms for selected CI reference wave functions with core electrons uncorrelated. Consider the expression for local energy given in Eq. 5

\[
E_L[n] = \sum_n \frac{\langle n | H | m \rangle}{\langle n | \psi^{(0)} \rangle} \frac{\langle m | \psi^{(p)} \rangle}{\langle m | \psi^{(0)} \rangle}.
\]

The walker \( |n\rangle \) belongs to either the CAS or the FOIS. The determinants \( |m\rangle \) are generated from \( |n\rangle \) through the Hamiltonian. Note that only those \( |m\rangle \)'s that are at most doubly excited from the CAS have a non-zero overlap with the wave function and thus only these excitations need to be generated. If the resulting \( |m\rangle \) is not in the CAS, we again need to generate excitations.
from this determinant using the Hamiltonian to calculate its overlap with the wave function (cf. Eq. 6). The number of determinants that need to be generated from $|m\rangle$ is significantly less than the number of all determinants connected to it since they have to be in the CAS to have a non-zero overlap with $|\phi_0\rangle$. We use the heat-bath algorithm\textsuperscript{3} to generate all excitations efficiently. The determinants in the reference $|\phi_0\rangle$ are stored in a hash table, so the overlap of a determinant with it can be calculated in constant time on average. Because this method avoids calculation of the expensive RDMs, its memory cost is negligible compared to the deterministic algorithm. Similar considerations apply to the quantities sampled in SC-NEVPT2(s), with the exception that in this case, the first set of excitations are generated using Dyall’s Hamiltonian instead of the full system Hamiltonian. This implementation can be extended to correlate core electrons and to work with other kinds of reference wave functions. Details of how this can be accomplished will be presented in a forthcoming publication.

3. RESULTS

In this section, we will present applications of SC-MRCI(s) and SC-NEVPT2(s) with a selected CI reference to demonstrate its utility in treating multireference problems quantitatively. We compare our energies to Celani-Werner (CW) MRCI energies obtained using MOLPRO,\textsuperscript{80} version 2019.1. We used PySCF\textsuperscript{81} to generate Hamiltonian integrals. The selected CI program Dice\textsuperscript{3,4,14} was used to obtain the determinants in the CASSCF wave function.

We report the computational timings for SC-MRCI(s) calculations of hydrogen chains of increasing length and compare them with CW-MRCI. We then present potential energy curves and spectroscopic constants for a few diatomic molecules. Finally, we analyze the efficacy of the Davidson correction for achieving approximate size-consistency.

3.1. Hydrogen chain

MRCI energies were calculated for open hydrogen chains of increasing lengths in the 6-31g basis set. The bond length was set to 2 Bohr in all calculations. The active space consisting of the 1s orbitals on each hydrogen was used. Fig. 1 presents computational times, and Table 1 shows the ground state energies for SC-MRCI(s) and CW-MRCI.

AMSGrad was used to optimize the variational energy and to obtain the converged SC-MRCI(s) wave function. It usually requires fewer AMSGrad iterations to converge to the final result if more stochastic samples are used. In our numerical experiments, we have found that using enough samples to obtain energies with an error of $\sim 10$ mE$_h$ in the first iteration leads to smooth optimization in most cases. 2400 stochastic samples were enough to achieve this accuracy for all chain lengths considered here. We progressively increased the number of stochastic samples as the wave function approached convergence, and all the reported SC-MRCI(s) energies here have a stochastic error of less than 1 mE$_h$. Calculations were performed on a single compute node with two Intel® Xeon® E5-2680 v3 processors (2.5 GHz) and 116 GB memory. SC-MRCI(s) calculations were parallelized over all available cores using MPI, while MOLPRO calculations were performed serially since a parallel implementation is not available. It is apparent from Fig. 1 that although CW-MRCI is very efficient for smaller active spaces, its scaling with the size of the active space is worse compared to SC-MRCI(s). This can be attributed to the use of uncontracted excitations for certain semi-internal excitation classes in CW-MRCI. As a result, for even the moderately sized H$_{14}$ chain, SC-MRCI(s) achieves a performance similar to CW-MRCI. For the H$_{16}$ chain, we were unable to perform the CW-MRCI calculation on a single node, while the SC-MRCI(s) calculation took only about three hours. We note that CW-MRCI can be
performed a final single point calculation with sufficient
converged in about 15-20 AMSgrad iterations. We then
each AMSGrad iteration. In all cases, the optimization
stochastic samples in all SC-MRCI(s) calculations for
frozen in all correlated calculations. We used 48,000
and (10e,8o), respectively. The 1s core electrons were
curves of HF, N
vorably to the deterministic methods for even small to
mentation, the stochastic algorithm might compare fa-
matrix product states. With improvements to our imple-
such as symmetry projected Jastrow mean-field and ma-
trix product states. With improvements to our imple-

3.2. Diatomic molecules

We have calculated the ground state potential energy
curves of HF, N$_2$, and CO molecules in the cc-pVTZ basis
using full-valence active spaces of sizes (8e,5o), (10e,8o),
and (10e,8o), respectively. The 1s core electrons were
frozen in all correlated calculations. We used 48,000
stochastic samples in all SC-MRCI(s) calculations for
each AMSGrad iteration. In all cases, the optimization converged in about 15-20 AMSgrad iterations. We then performed a final single point calculation with sufficient stochastic samples to achieve an error less than 0.2 mE$_h$. We have found that the number of stochastic samples needed to obtain a given accuracy scales roughly linearly with the number of variables in the wave function. For SC-NEVPT2(s) calculations, $9.6 \times 10^6$ stochastic samples were used. The greater number of stochastic samples was needed partly because the second-order correction to the energy is a non-linear function of $E_i^{(k)}$ (see Eq. 15), which is itself calculated stochastically. As a result, in addition to a stochastic error, the SC-NEVPT2(s) energy also has a systematic bias, as has been investigated in other QMC methods previously.$^{52,53}$ However, with the relatively large number of stochastic samples used here, we find that the systematic bias is smaller than the stochastic noise. We confirmed this by performing 50 independent energy calculations at one geometry for each molecule. The standard deviation of the resulting distribution of energies was less than 0.3 mE$_h$ and the average was found to be within one standard deviation of the deterministic SC-NEVPT2 energy.

| Molecule | Method          | $r_e$ (au) | $\omega_p$ (cm$^{-1}$) | $\omega_x e$ (cm$^{-1}$) |
|----------|----------------|-----------|------------------------|--------------------------|
| HF       | SC-NEVPT2      | 1.747     | 4203                   | 77                       |
|          | SC-MRCI+Q(s)   | 1.743     | 4212                   | 80                       |
|          | CW-MRCI+Q     | 1.744     | 4182                   | 83                       |
| $N_2$    | SC-NEVPT2      | 2.090     | 2327                   | 14                       |
|          | SC-MRCI+Q(s)   | 2.090     | 2320                   | 14                       |
|          | CW-MRCI+Q     | 2.089     | 2330                   | 14                       |
| CO       | SC-NEVPT2      | 2.151     | 2135                   | 13                       |
|          | SC-MRCI+Q(s)   | 2.149     | 2154                   | 19                       |
|          | CW-MRCI+Q     | 2.150     | 2141                   | 13                       |

Table 2 shows the spectroscopic constants $r_e$, $\omega_p$, and $\omega_x e$ for these diatomic molecules obtained using MOLPRO. These are calculated by fitting the potential energy curve with a high-degree polynomial. To estimate the errors in the constants for SC-MRCI+Q(s), we performed a Monte Carlo analysis by fitting to energy values obtained by adding normally distributed noise, with a standard deviation chosen to match the error estimate on each data point. Sufficient samples were used so that the average values reported in the table are converged to all the digits shown. Because we do not have precise error estimates for the SC-NEVPT2(s) energies here, we opted to use deterministic SC-NEVPT2 values for these calculations. The values of constants are in excellent agreement with each other. The NP errors do not appear to affect these constants much.

Table 3 shows the size-consistency errors for these methods in the nitrogen molecule. In this case, all stochastic CI energies were converged to an accuracy of 0.2 mE$_h$. SC-NEVPT2(s) is exactly size consis-
tent (within statistical error) as expected. CW-MRCI and SC-MRCI(s) have large size-consistency errors which arise due to the same reasons as in the single-reference CI case. The Davidson correction does seem to remedy this issue to a large extent. The relatively small NP and size-consistency errors in the SC-MRCI+Q(s) and SC-NEVPT2(s) methods are encouraging and indicate that it may be feasible to treat problems with a large number of virtual orbitals using our framework.

TABLE 4: Size-consistency errors for N\textsubscript{2} calculated as the difference between the energy of two well separated atoms and twice the energy of a single atom.

| Method          | ∆E (mE\textsubscript{h}) |
|-----------------|--------------------------|
| SC-NEVPT2(s)    | 0.0                      |
| CW-MRCI         | 7.6                      |
| CW-MRCI+Q       | 1.0                      |
| SC-MRCI(s)      | 8.0                      |
| SC-MRCI+Q(s)    | 2.1                      |

4. CONCLUSIONS

In this work, we have presented stochastic formulations of SC-MRCI and SC-NEVPT2 methods that avoid the requirement of storing expensive high-order active space RDMs. The need to calculate and store these RDMs has been a major bottleneck in calculating dynamic correlation in multireference theories, especially when active spaces are large. Using benchmark calculations on hydrogen chains and diatomic molecules, we have argued that the stochastic method, presented here, represents an attractive alternative to the deterministic methods. It outperforms the corresponding deterministic method even with active spaces that are as small as 14 orbitals.

Our work also highlights the accuracy of the strongly contracted wave functions, which is in agreement with previous work. However, even with this relatively small loss of accuracy, the use of strong contraction in deterministic algorithms is often not recommended because the saving in computational time relative to internal or partial contraction is negligible. This metric drastically changes in the stochastic approach presented here, because the optimization problem one needs to solve for strong contraction is significantly easier than when partial or internal contraction are used. Thus with stochastic methods, our recommendation is to use strong contraction and only resort to internal contraction when it is known that the former is likely to fail.

This work will be extended in several directions. All calculations presented here have used the frozen core approximation. We are working on an efficient implementation of excitation classes that correlate core electrons. It will be interesting to see how the stochastic method performs with other reference wave functions, such as matrix product states and symmetry-projected Jastrow mean field states. A problem that we have not discussed here is that the strongly contracted wave functions are not invariant to unitary transformations in the virtual orbitals. Our preliminary results indicate that the results are most accurate when canonical CASSCF virtual orbitals are used, however, the efficiency of calculation suffers when such delocalized orbitals are used. More work is needed to determine what kind of virtual (and core) orbitals will lead to the best results. The fact that our formulation can be used with many different active-space wave functions and places virtually no restrictions on the size of the active or virtual spaces, raises the exciting prospect of performing multireference calculations on large systems that are beyond the reach of current methods.

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