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ABSTRACT

We implement Epstein–Nesbet perturbative corrections in the third-order for the initiator approximation of the configuration space quantum Monte Carlo. An improved sampling algorithm is proposed to address the stochastic noise of the corrections. The stochastic error for the perturbative corrections is considerably larger than that for the reference energy, and it fails to provide reasonable results unless a very long imaginary time integration is performed. The new sampling algorithm accumulates rejected walkers from multiple independent steps to cover a larger portion of the secondary space. The performance of the perturbative corrections is demonstrated for small molecules.

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I. INTRODUCTION

Electronic structure methods are used to obtain accurate energies and properties of many-electron systems. A number of approaches in electronic structure theory have been proposed to incorporate electron correlation into the wave function in order to provide accurate descriptions of fermionic systems. Quantum Monte Carlo (QMC) in the configuration space based on the projector ansatz of the imaginary-time (ITE) evolution,

$$\Psi(\tau) = e^{-\tau(\hat{H}-E)}\Psi_0, \tag{1}$$

is being popularly used to obtain high-quality wave functions commencing from a suitable initial wave function, Ψ_0, which is usually chosen to be the Hartree–Fock (HF) solution. Full configuration interaction QMC (FCIQMC)[1–3] in the discrete space of Slater-determinants mitigates the memory requirement problem for the large-scale diagonalization of systems that are out of reach using deterministic approaches. Model space QMC (MSQMC)[4–6] can be used to calculate excited states by utilizing the effective Hamiltonian formalism. Nevertheless, the size of the sampled space grows combinatorially with the system size, leading to the exponential growth of the walker population.

The sign-problem of QMC in the configuration space is addressed by the initiator adaptation,[2] in which determinants with walker population less than a preset initiator threshold T_I are labeled as non-initiator determinants, and walkers that spawn from these determinants onto unoccupied determinants are discarded to truncate the sampled space in a systematically improvable manner. However, the initiator approach leads to a size-inconsistency error as observed in a deterministic CI in a limited configuration space, which becomes significant with an increasing number of electrons. The size-inconsistency error is more serious than the truncation errors when using size-extensive theories such as many-body perturbation and coupled-cluster (CC) because a truncated CI reduces to a mean field description in the thermodynamic limit. To ameliorate this feature, stochastic coupled-electron pair approximation (CPEA) corrections have been introduced recently.[6] The adaptive shift method[7] is also considered to be a stochastic CEPA variant that is used to reduce the size-inconsistency error with the local shift parameter. CC-QMC[8,9] exploiting the exponential ansatz is an *a priori* size-consistent approach, and a stochastic counterpart of the

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recent development of a selected CC in the entire Hilbert space, the so-called full CC reduction (FCCR),[10] may provide a useful mean for this purpose.

An alternative method for reducing the initiator error is the use of a second-order Epstein–Nesbet (EN2) correction,[11] which is closely related to the recently developed stochastic perturbative corrections for selected CI[12,13] and the density matrix renormalization group.[14] The second-order correction is accumulated based on a formula that contains the square of the rejected walkers, which could be heavily biased when samples from the same dataset are used. This bias can be avoided by the replica trick[15] for accumulating the correction by presuming that the same determinants in the interacting space are sampled in the given time step. The event of coinciding indices of the rejected walkers by the initiator criteria is very rare, resulting in severe noise in the perturbation energy. Recently, a novel algorithm to mitigate the stochastic error in the second-order correction was proposed.[16] This was enabled by the introduction of preconditioners, an increased time step, and multiple spawning events per walker.

In the present paper, we introduce the third-order EN correction to the initiator approximation to further improve the accuracy of the final electronic energy by using the general perturbation theory. We also develop an algorithm for improving the sampling efficiency of the perturbative corrections by collecting more samples of the rejected walkers. The remainder of this paper is structured as follows. The equations related to the wave function sampled using the initiator adaptation and EN perturbation theory are examined in Sec. II. The mathematical background of the dependency between the standard deviation and the new sampling algorithm is also presented. Section III summarizes the numerical results of the initiator errors with the perturbative corrections in the third-order.

II. THEORY

In the EN perturbation theory, the Hamiltonian operator is expressed as a sum of the zeroth order Hamiltonian ($\hat{H}_0$) and the perturbation operator ($\hat{V}$),

$$\hat{H} = \hat{H}_0 + \hat{V}. \tag{2}$$

$\hat{H}_0$ contains diagonal and off-diagonal elements in the variational subspace ($\mathcal{V}$) and the diagonal elements from the interacting secondary space,

$$\hat{H}_0 = \sum_{ij\in\mathcal{V}} H_{ij}|D_i\rangle\langle D_j| + \sum_{a\notin\mathcal{V}} H_{aa}|D_a\rangle\langle D_a|. \tag{3}$$

The wave function in the variational space ($|\psi^{(0)}\rangle$) is corrected by the contributions of the first-order wave function. The second- and third-order energy corrections are

$$E^{(2)} = \sum_{a\notin\mathcal{V}} \frac{\left(\sum_{i\in\mathcal{V}} H_{ia}c_i\right)^2}{\Delta_a}, \tag{4}$$

$$E^{(3)} = \sum_{a,b\notin\mathcal{V}} \frac{\left(\sum_{i\in\mathcal{V}} H_{ia}c_i\right)H_{ab}\left(\sum_{j\in\mathcal{V}} H_{jb}c_j\right)}{\Delta_a\Delta_b}, \tag{5}$$

where the denominator,

$$\Delta_a = E_{\mathrm{var}} - H_{aa}, \tag{6}$$

contains the variational energy that can be calculated using the usual Rayleigh quotient,

$$E_{\mathrm{var}} = \frac{\langle\psi^{(0)}|\hat{H}|\psi^{(0)}\rangle}{\langle\psi^{(0)}|\psi^{(0)}\rangle}. \tag{7}$$

A stochastic algorithm for $E^{(2)}$ in the initiator approach was developed by Blunt.[11] The basic idea for the algorithm is that the expected contribution to a determinant outside $\mathcal{V}$ is proportional to the average number of removed walkers on the determinant because of the initiator criteria, $S_a \propto \sum_{i\in\mathcal{V}} H_{ia}c_i$, supposing $\mathcal{V}$ to be the occupied space in the initiator approach. Then, a stochastic estimate of $E^{(2)}$ to correct the initiator error at imaginary time τ can be expressed as

$$E^{(2)}(\tau) = N_\tau \sum_{a\notin\mathcal{V}} \frac{S_a^{(1)}(\tau)S_a^{(2)}(\tau)}{\Delta_a}, \tag{8}$$

with the normalization

$$N_\tau = \frac{1}{(L_2^{\mathrm{walk}}(\tau))^2(\Delta\tau)^2}, \tag{9}$$

$$L_2^{\mathrm{walk}}(\tau) = \sqrt{\sum_i N_i^{(1)}(\tau)N_i^{(2)}(\tau)}, \tag{10}$$

where $\Delta\tau$ is the time step for QMC, $N_i^{(1)}(\tau)$ is the walker population of determinant i, $S_a^{(1)}(\tau)$ is the instantaneous contribution to S_a (number of removed walkers at τ due to the initiator criteria), and $E_{\mathrm{var}}(\tau)$ is the instantaneous energy of the wave function in the variational space at τ. The upper index of $N_i^{(1)}$ or $S_a^{(1)}$ indicates a need for two independent populations (original and replica) to eliminate the bias in the squared quantities. The importance of using a variational estimator over the standard projected estimator for approximate wavefunctions has been suggested for E_{var}.[11] The variational estimator is calculated in a direct manner without using reduced density matrices.[16] By discerning that the discarded walkers, which do not fulfill the initiator criteria, are proportional to $S_a(\tau)$, the initiator error is corrected using these walkers.[11] We can proceed by introducing the expression for the third-order energy in an analogous fashion,

$$E^{(3)}(\tau) = N_\tau \sum_{a,b\notin\mathcal{V}} \frac{S_a^{(1)}(\tau)H_{ab}S_b^{(2)}(\tau)}{\Delta_a\Delta_b}. \tag{11}$$

It has been considered that the result of the third-order perturbation theory is less sensitive to the choice of $\hat{H}_0$ than the second-order one.[17]

The second- and third order energy contributions are accumulated only when there is a disposal of walkers both from the original and replica populations. Depending on the size of the secondary space and the number of walkers employed, the sampling of the

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terms in Eqs. (8) and (11) can be extremely sparse. The sampling by the discarded walkers is generally very poor even at the equilibrium of the walker population because there is little overlap between $S_a^{(1)}(\tau)$ and $S_a^{(2)}(\tau)$, and the fluctuation of the energy corrections becomes considerably severe.

Our stochastic algorithm is implemented in such that multiple samples are averaged for the perturbative collections. In other words, we choose to collect discarded walker samples into $S_a^{(1)}(\tau)$ and $S_b^{(2)}(\tau)$ from N_m multiple micro steps to calculate $E^{(2)}$ and $E^{(3)}$ less frequently using more samples. The new sampling introduces a change in N_τ as follows:

$$N_\tau' \Leftarrow \frac{N_\tau}{N_\mathrm{m}^2}, \tag{12}$$

and the contributions for $E^{(2)}$ and $E^{(3)}$ are accumulated using N_τ' instead of N_τ, where $L_2^{\mathrm{walk}}(\tau)$ is taken from one of the N_m iterations assuming the stationarity of the walker populations in $\mathcal{V}$. Collecting samples from multiple micro steps only results in a small memory overhead without requiring additional computational costs. The calculation of $E^{(2)}$ scales as $O(N_\mathrm{m})$; however, to check the coincidence of indices, $O(N_\mathrm{m}\log N_\mathrm{m})$ operation must be performed to sort the discarded walkers, and the use of a hash table is expedient for this purpose. The cost for $E^{(3)}$ is quadratic to N_m, and collecting too many samples can cause a delay in the calculation.

The fluctuation of the energy corrections strongly depends on N_m, for which we store the samples of the rejected walkers outside $\mathcal{V}$. The summations of the corrections,

$$E^{(2)}(\tau) = N_\tau' \sum_{a\notin\mathcal{V}} \frac{S_a^{(1)}(\tau)S_a^{(2)}(\tau)}{\Delta_a} \tag{13}$$

and

$$E^{(3)}(\tau) = N_\tau' \sum_{a,b\notin\mathcal{V}} \frac{S_a^{(1)}(\tau)H_{ab}S_b^{(2)}(\tau)}{\Delta_a\Delta_b}, \tag{14}$$

are performed over the lists of the rejected wakers, $\{\Psi_{a_1},\Psi_{a_2},\ldots,\Psi_{a_i}\}$, whose dimensions are proportional to N_m. Therefore, the stochastic error of the corrections decays as the inverse square root of the number of samples, $\sigma \propto \frac{1}{\sqrt{N_\mathrm{m}}}$. The corresponding EN energies with the corrections are given by

$$E_{\mathrm{EN2}} = E_{\mathrm{var}} + E^{(2)}, \tag{15}$$

$$E_{\mathrm{EN3}} = E_{\mathrm{var}} + E^{(2)} + E^{(3)}. \tag{16}$$

III. NUMERICAL EXAMPLES

To demonstrate the efficiency of the new sampling, we perform calculations on the N_2 molecule in the cc-pVDZ basis set to measure the standard deviation of the second order energy correction with different N_m. We employ the MSQMC algorithm[4,6] with a model space comprising only a single HF determinant. In this case, the walker population on the model space determinant is fixed to the booster weight N_b[4] and is included in the summation for $L_2^{\mathrm{walk}}(\tau)$, while the corresponding occupation fluctuates in the FCIQMC algorithm. The instantaneous energy is integrated over the ITE for a duration τ commencing the integration at τ_1. The result is depicted in Fig. 1. It is clearly shown that the stochastic error decreases with increasing N_m. The deviation is steadily reduced up to N_m = 100, and the gain becomes smaller for larger N_m. Since there is a small overhead for accumulating the third-order contribution, we use N_m = 5, which is considered to be a reasonable value in practice.

The calculations are presented here to demonstrate the applicability of the perturbative corrections for small molecules. The deterministic Møller–Plesset (MP) perturbation series and CC singles doubles with perturbative triples, CCSD(T), are used for comparison. The frozen core approximation is employed, and three independent calculations are performed for the standard deviation. Thus, the error bars indicated in the following may have some uncertainty because of the limitation of the estimate. First, we focus on the result of H_2O in the cc-pVDZ basis set with the HF optimized geometry in Fig. 2. The EN2 energy is negatively deviated from FCI for a large initiator threshold T_I, while EN3 recovers a large amount of the error of EN2. Note that the present range of T_I is under a severe condition compared with the standard initiator adaptation, in which EN2 is sufficiently accurate, as shown, for the same system in a slightly larger basis.[11] With N_b = 250 and T_I = 6 in this calculation, the number of walkers in equilibrium are approximately 3000, which is sufficient for obtaining the near FCI energy for EN3. The number of walkers increases to approximately 6500 if the initiator threshold T_I is tightened to 3. Since EN2 at T_I = 3 exhibits the same order of accuracy as EN3 at T_I = 6, it is more expedient to use the third-order correction instead of reducing T_I, which would cause a significant increase in the computational cost with the larger number of walkers and memory requirement.

The N_2 molecule, possessing a triple bond at equilibrium geometry, has been used as a benchmark in studies.[18–20] Its tendencies are

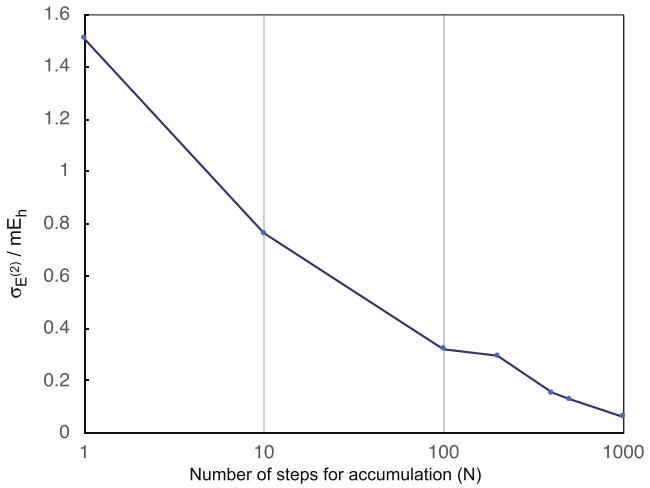

FIG. 1. Standard deviation of the second-order energy vs N_m. The calculation on the N_2 molecule in the cc-pVDZ basis set is carried out with r_{NN} = 1.120 13 Å, N_b = 250, T_I = 12, τ = 100 a.u., and τ_1 = 60 a.u. Eight independent calculations with different random number seeds are performed to calculate the standard deviation σ.

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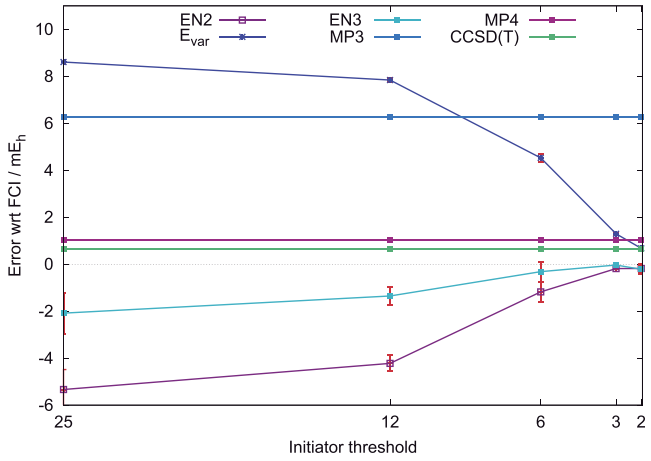

FIG. 2. Errors of E_{EN2} and E_{EN3} for H_2O with respect to FCI, compared with MP3, MP4, and CCSD(T) as functions of T_I. The calculation is performed for N_b = 250, N_m = 1, τ = 2000 a.u., and τ_1 = 600 a.u. in cc-pVDZ. The largest measured standard deviations of the initiator energies are 0.2 mE_h and 0.9 mE_h for E_{EN2} and E_{EN3}, respectively. The FCI energy is −76.2417E_h.

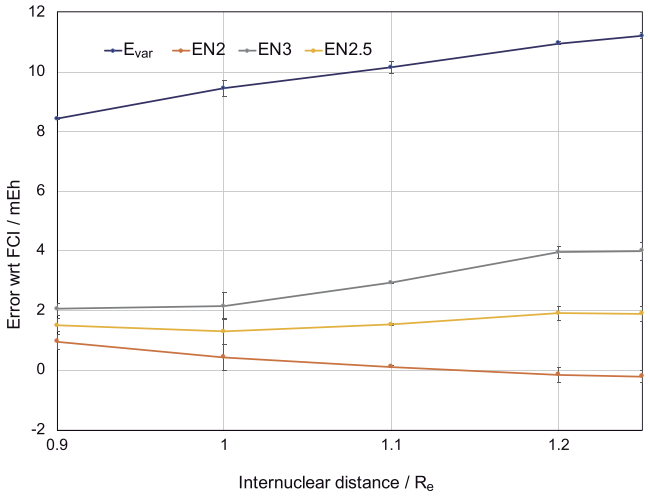

FIG. 4. Errors in the potential energies with respect to FCI for N_2 in the vicinity of R_e = 1.120 13 Å as functions of the bond length in cc-pVDZ. The standard deviations of QMC are indicated by the vertical lines. The parameters for QMC are T_I = 6, N_b = 250, N_m = 5, τ = 1000 a.u., and τ_1 = 600 a.u.

similar to those of E_{EN2} and E_{EN3}, as shown in Fig. 3. The EN2 result is close to the FCI for this system, although most of the energy points are below FCI revealing a somewhat irregular profile. In contrast, the convergence of E_{EN3} is more systematic from above FCI with the tightened initiator threshold T_I. When changing T_I from 3 to 2, the total number of walkers increases approximately from 12 000 to 25 000. The errors in the potential energy curves with the initiator threshold T_I = 6 in the vicinity of the equilibrium distance are shown in Fig. 4. The initiator error in E_{var} increases as the nitrogen atoms are moved away from the equilibrium geometry, presumably because a single Slater-determinant is used in the model space for the N_b constant MSQMC simulations. The magnitude of the EN2 correction increases with increasing r_{NN}, while the effect of EN3 is inclined to be in the opposite direction. An offset of the second- and third-order effects is often observed, e.g., for the interaction energies of dispersion-bound complexes. A damped version of the perturbation theory has improved this situation considerably.[21,22] The nonparallelity errors (NPEs) of E_{var}, EN2, and EN3 are 2.8, 1.2, and 1.9 mE_h. EN2.5, an average of EN2 and EN3, considerably reduces NPE to 0.6 mE_h. The errors of EN2 are overall smaller than those of EN3 in Fig. 3, although the performances of the perturbative corrections are dependent on the system and T_I. Moreover, the reference and perturbation spaces are not strictly orthogonal because of the fluctuation of the initiators, which can also lead to some uncertainty in the performance. Further investigations with higher-order corrections such as E_{EN4} with more challenging applications are reserved for future studies.

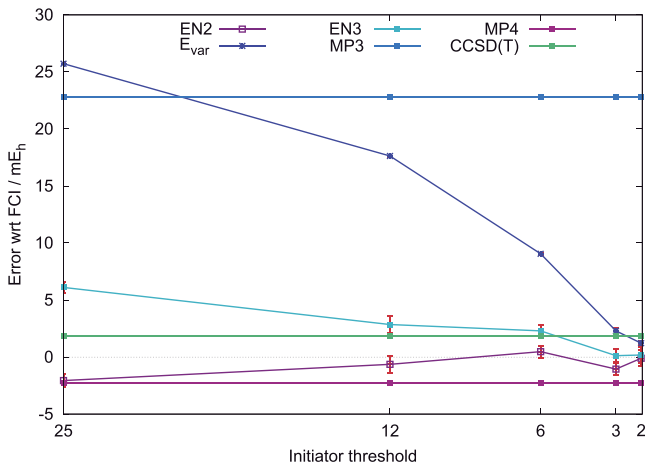

FIG. 3. Errors of E_{EN2} and E_{EN3} for N_2 with respect to FCI, compared with MP3, MP4, and CCSD(T) as functions of T_I. The calculation is performed for r_{NN} = 1.120 13 Å, N_b = 250, N_m = 1, τ = 2000 a.u., and τ_1 = 600 a.u. in cc-pVDZ basis. The largest measured standard deviations of the initiator energies are 0.3 mEh and 0.8 mEh for E_{EN2} and E_{EN3}, respectively. The FCI energy is −109.2783E_h.

IV. CONCLUSIONS

The initiator adaptation addresses the sign-problem and provides a powerful tool for sampling the wave function in a large active space, in which the exact diagonalization of the FCI matrix is impossible even with the latest supercomputers. Nevertheless, the dimension of the secondary space in a realistic calculation is extremely large, hindering the accurate treatment of the system. Therefore, the benefit of EN perturbation theory has been manifested in the initiator adaptation, and it seems to recover the vast of the residual correlation to fix the size-inconsistency error. Besides a large stochastic error, the calculation of E_{EN2} is not an overhead as the calculation can be performed in a parallel manner without

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extra inter-process communications of the data. E_{EN3} systematically increases the accuracy of the correction at the cost of introducing more terms in the summation. For each of the terms in $E^{(3)}$, the Hamiltonian matrix elements appear in the innermost loop. Increasing the size of the active space limits the applicability of the method mostly because supercomputers have limited memories and available run times. Thus, it is likely that the use of perturbative corrections for the initiator approximation is overall more advantageous than tightening the initiator threshold as the system size increases. The present implementation for the perturbative corrections is pilot and unparallelized. However, a high parallel efficiency for E_{EN3} would be obtained by a proper implementation by keeping the entire $S_a^{(1)}(\tau)$ [or $S_b^{(2)}(\tau)$] in each of the processes; this does not require a large amount of additional memory. Other important developments include a stochastic algorithm for higher-order corrections. One promising solution could be using a small number of walkers in QMC and to recover the remaining correlations by the corrections having been described in this paper.

We have also introduced a scheme to collect multiple samples and accumulate the corrections to reduce the stochastic error for the perturbative corrections. In many of the calculations, only a small fraction of the Hilbert space was sampled by using a few hundred walkers on the reference determinant and by choosing a fairly high initiator threshold. A method for excluding less important contribution is essential, and a truncation without circumspection leads to unphysical results as observed in the stochastic perturbation theory in a limited configuration space.[23]

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DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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