Stochastic many-body perturbation theory for electron correlation energies

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 Treating electron correlation more accurately and efficiently is at the heart of the development of electronic structure methods. In the present work, we explore the use of stochastic approaches to evaluate high-order electron correlation energies, whose conventional computational scaling is unpleasantly steep, being \( O(N^{n+3}) \) with respect to the system size \( N \) and the perturbation order \( n \) for the Moller-Plesset (MP) series. To this end, starting from Goldstone’s time-dependent formulation of \textit{ab initio} many-body perturbation theory (MBPT), we present a reformulation of MBPT, which naturally leads to an Monte Carlo scheme with \( O(n^3 NN + f(n)) \) scaling at each step, where \( f(n) \) is a function of \( n \) depending on the specific numerical scheme. Proof-of-concept calculations demonstrate that the proposed quantum Monte Carlo algorithm successfully extends the previous Monte Carlo approaches for MP2 and MP3 to higher orders. Therefore, for the first time the Goldstone’s time-dependent formulation is made useful numerically for electron correlation energies, not only being purely as a theoretical tool.

I. INTRODUCTION

The development of accurate and efficient methods for electron correlations is an enduring frontier in quantum chemistry. For weakly correlated systems, the many-body perturbation theory (MBPT) and the coupled-cluster (CC) theory have been well-established as the standard tools due to their high accuracy and size extensity. The later property is essential for large systems. However, their unfavorable scalings make the application to situations that require high accuracy still a significant challenge. Important situations include the studies of polymorphism of pharmaceutical solids and relative stabilities of different structures of water clusters, which typically require an accuracy of 0.1 kcal/mol. Although local correlation methods with reduced scalings have been significantly advanced in recent years, the lack of a method to benchmark their accuracies for large systems is also a problem to be solved. Due to its low scaling \( O(N^3) \) with \( N \) being the system size, the diffusion quantum Monte Carlo (QMC) algorithms in \textit{ab initio} quantum chemistry is gaining increasing popularity for large systems in recent years. However, the errors introduced by the fixed node approximation also require careful calibrations. Therefore, there is clearly still a need for developing methods with guaranteed accuracy for large systems even in the weakly correlated regime.

Motivated by various recent developments of quantum Monte Carlo (QMC) algorithms in \textit{ab initio} quantum chemistry and condense matter physics, in the present work, we explore the possibility of using stochastic approaches to evaluate high-order electron correlation energies. Specifically, we will present a reformulation of standard MBPT into a general mathematical form, which is more suitable for Monte Carlo evaluations. In sharp contrast to the steep scaling \( O(N^{n+3}) \) of the conventional algorithm for the \( n \)-th order in the Moller-Plesset (MP) series, the resulting QMC algorithm for evaluating the correlation energies scales as \( O(N^3) \) with respect to the system size. Although it is known that MBPT is less robust than CC and may fail to converge even for simple weakly correlated systems, having the ability to compute high order MP\( n \) energies for large systems is still valuable. Because the convergence issue can be overcome when more information about the behaviors of MP\( n \) is available, which has been demonstrated for small molecules via resummation techniques. In view of its low scaling, the proposed QMC algorithm may potentially open up the possibility to compute large systems (or small systems but with very large basis sets) with high accuracy without resorting to any local approximation.

II. RECAPITULATION OF MBPT

To begin with, we briefly recapitulate the standard MBPT in Goldstone’s time-dependent formulation[23], which is the starting point of our reformulation of MP\( n \) correlation energies. For simplicity, we will focus on the MP partition, viz., \( \hat{H} = \hat{H}_0 + \hat{V} \) with \( \hat{H}_0 = \sum_p \varepsilon_p \hat{a}_p \hat{a}_p^\dagger \), where the zeroth order state is the canonical Hartree-Fock (HF) reference \( |\Phi_0\rangle = |\Phi_{\text{HF}}\rangle \) and \( \hat{V} = \hat{V}_{\text{HF}} - \hat{V}_{\text{HF}} \). The Goldstone’s linked-cluster theorem states that the \((n+1)\)-th order correlation energy is given by

\[
E_{n+1} = \lim_{\epsilon \to 0} \frac{(-i)^n}{n!} \int_{-\infty}^{0} dt_1 \cdots dt_n e^{-\epsilon(|t_1| + \cdots + |t_n|)} \langle \Phi_0 | \hat{V}(t_1) \hat{V}(t_2) \cdots \hat{V}(t_n) | \Phi_0 \rangle, \tag{1}
\]

where \( \hat{V}(t) = e^{i\hat{H}_0 t} \hat{V} e^{-i\hat{H}_0 t} \) is the corresponding perturbation operator in the interaction picture and the subscript ‘c’ indicates the connected parts.

Proof-of-concept calculations demonstrate that the proposed quantum Monte Carlo algorithm successfully extends the previous Monte Carlo approaches for MP2 and MP3 to higher orders. Therefore, for the first time the Goldstone’s time-dependent formulation is made useful numerically for electron correlation energies, not only being purely as a theoretical tool.
Coulomb interaction, $\hat{V}_{\text{ee}}$ can be written as

$$\hat{V}_{\text{ee}} = \frac{1}{2} \int dx_1 dx_2 v(x_1, x_2') \hat{\psi}^\dagger(x_1) \hat{\psi}^\dagger(x_1') \hat{\psi}(x_1') \hat{\psi}(x_1)[2]$$

where $x_1 \equiv (\sigma_1, r_1)$ and $x_2' \equiv (\sigma_1', r_1')$ are composite indices for spin and spatial variables, $v(x_1, x_2') = \delta_{\sigma_1, \sigma_1'}/|r_1' - r_1|$, and the integration over $x_1$ implies both a summation over spin $\sigma_1 \in \{\alpha, \beta\}$ and an integration over spatial coordinates $r_1' \in \mathbb{R}^3$. For brevity, we also introduce a compact notation $\hat{\psi}^\dagger(1) \equiv \hat{\psi}^\dagger(x_1, t_1)$ to represent operators in the interaction/Heisenberg picture by defining $1 \equiv (t_1, \sigma_1, r_1)$.

Since $\hat{H}_0$ is quadratic, the (physical) vacuum expectation value in Eq. (1) can be evaluated using the Wick’s theorem, which implies a factorization of high-order noninteracting Green’s functions into a sum over products of one-body Green’s function (propagators)

$$G^0(1, \cdots , n; 1', \cdots , n') \equiv (-i)^n \Phi_0[\hat{T}^\dagger \hat{\psi}(1) \ldots \hat{\psi}(n) \hat{\psi}^\dagger(n') \ldots \hat{\psi}^\dagger(1)]\Phi_0 = \det(G^0_n), \quad (3)$$

where $G^0_n$ is an $n$-by-$n$ matrix with entries $(G^0_n)_{k,l} \equiv G^0(k,l) = -i \langle \hat{\Psi}_0[\hat{T}^\dagger \hat{\psi}(k) \hat{\psi}^\dagger(l)] \rangle \Phi_0$. Applying the Wick’s theorem (3) in Eq. (1) and expanding the determinant, each product can be represented by a Feynman (Goldstone) diagram either connected or disconnected, and the linked cluster theorem states that only those connected parts contribute to $E_{n+1}$. This is the standard way to derive Feynman diagrams in MBPT. However, for our purpose, we will keep Eq. (3) in its unexpanded form. The central result of this work is to show that for the ground state (a more precise condition will be given in Sec. III), Eq. (1) can be recast into

$$E_{n+1} = \left(\frac{-1}{n!}\right) \int_{-\infty}^{0} dr_1 \cdots dr_n \langle \Phi_0 | \hat{V}_{\text{f}}(0) | \hat{V}_{\text{f}}(\tau_1) \cdots \hat{V}_{\text{f}}(\tau_n) \rangle \Phi_0, \quad (4)$$

where $\hat{V}_{\text{f}}(\tau) = e^{\tau(\hat{H} - \mu \hat{N})} \hat{V} e^{-\tau(\hat{H} - \mu \hat{N})}$ and the analog of "chemical potential" $\mu$ is an arbitrary constant here.

The form (4) is more computationally appealing, since it only involves real quantities, whereas Eq. (1) involves oscillating complex quantities arising from $e^{\pm \hat{H}\omega}$, which will make the later stochastic evaluation more challenging in general. Besides, the unpleasant adiabatic factor $e^{-\tau[\hat{H}]}$ is also removed from Eq. (1).

There are several ways to derive Eq. (3), but the most obvious way is to consider the well-known time-independent expression derived from Eq. (1).

$$E_{n+1} = \left(\frac{-1}{n!}\right) \sum_{\{I\}} \left( V_{0I_1} \frac{1}{\omega_{I_1}} V_{I_1I_2} \frac{1}{\omega_{I_2}} \cdots \frac{1}{\omega_{I_n}} V_{I_n0} \right)_c \quad (6)$$

where $V_{I_1I_2} = \langle \Phi_{I_1} | \hat{V} | \Phi_{I_2} \rangle$ with $|\Phi_{I_1}\rangle$ being intermediate states, and $1/\omega_I \equiv 1/(E_I - E_0)$ represents the energy denominator. By performing a Laplace transform $1/\omega_I = \int_{-\infty}^{0} d\tau e^{\omega_I \tau}$ and reversing the derivation from time-dependent PT to time-independent PT (4), we can derive Eq. (5) from Eq. (6). However, two differences need to be noted.

First, the condition for the Laplace transform requires $\omega_I > 0$ for all intermediate states, and hence Eq. (5) is valid only for the case that $|\Phi_0\rangle$ is the ground state of $\hat{H}_0$, whereas Eq. (1) based on the Gell-Mann-Low theorem in principle also works for excited states. Since we are mainly focused on the ground state problem in this work, this condition is usually satisfied.

Second, in Eq. (5) we have introduced a parameter $\mu$, which formally corresponds to the chemical potential in finite temperature MBPT. But here it is completely arbitrary, as can be seen in Eq. (6), because as long as $\hat{V}$ does not change the particle number, $\mu$
will be exactly cancelled in taking energy differences in the denominator \(1/\omega\). However, for numerical convenience, we can choose it to be a value within the gap between the HOMO (highest occupied molecular orbital) and the LUMO (lowest unoccupied molecular orbital), e.g., \(\mu = \text{HOMO} + \text{LUMO}\) used in the present work, such that given \(|\Phi_0\rangle\), we have \(\varepsilon_i^\tau \equiv \varepsilon_i - \mu < 0\) for occupied orbitals and \(\varepsilon_a^\tau \equiv \varepsilon_a - \mu > 0\) for virtual orbitals. This will make the exponential factor in the imaginary time Green’s function \(G^\tau(k, l)\), appearing in the counterpart of Eq. (3), always smaller than one,

\[
G^\tau(k, l) = \theta(\tau_{kl})G^\tau_0(k, l) + \theta(-\tau_{kl})G^\tau_0(k, l),
\]

\[
G^\tau_0(k, l) = -\delta\sigma_\sigma \sum_n e^{-\varepsilon_{i}^\tau} \psi_{i\sigma}^*(\vec{r}_k)\psi_{n\sigma}^*(\vec{r}_l),
\]

\[
G^\tau_0(k, l) = \delta\sigma_\sigma \sum_i e^{-\varepsilon_i^\tau} \psi_{i\sigma}^*(\vec{r}_k)\psi_{n\sigma}^*(\vec{r}_l),
\]

where \(\tau_{kl} \equiv \tau_k - \tau_l\). The same trick was previously introduced in the Laplace-transformed MP2\(^{22}\).

Alternatively, the above results can be derived from Eq. (1) by analyzing each connected Goldstone diagram and performing an analytic continuation of the real time integration to the imaginary time. We will not go into the details, but just mention that the same condition \(\omega_i > 0\) in this case will come from the requirement to guarantee that the contour integral over the arc goes to zero.

### IV. Summation of Diagrams by Moment-Cumulant Relations

The next step is to express Eq. (6) into Eq. (4). Applying the imaginary-time analogy of Wick’s theorem (3) in Eq. (5), the expectation value \(\langle \Phi_0:\{\hat{V}_i(t_0)\hat{V}_i(t_1)\ldots\hat{V}_i(t_n)\}\rangle_{\Phi_0}\), for \(E_{n+1}\) will become \(\frac{1}{2\pi i} w_{n+1}\) det \((G^0_n)_{2n+2}\), where again the subscript ‘c’ is used to denote the connected contributions. For small \(n\), det \((G^0_n)_{2n+2}\) can be explicitly expanded, which corresponds to the use of Goldstone diagrams as employed in MC-MP2 (Monte Carlo MP2) and MC-MP3 by Hirata et al.\(^{10,11}\) However, this approach quickly becomes inefficient as \(n\) increases, since the number of diagrams increases factorially. While there are only 2 diagrams for MP2 and 12 diagrams for MP3, MP4 and MP5 have 300 and 13680 Goldstone diagrams,\(^{20,22}\) respectively. Recently, in the context of diagrammatic Monte Carlo, which samples all Feynman diagrams stochastically, a trick to sum all connected diagrams at order \(n\) was proposed by Rossiter\(^{13}\) by recursively subtracting disconnected contributions from determinants containing all diagrams. It has an exponential scaling \(O(2^n n^3 + 3^n)\), but is less than factorial and has allowed to sum diagrams at order as high as 10 for the Hubbard model\(^{13}\). The same recursive formula (vide post) can be applied to compute det \((G^0_n)_{2n+2}\) from det \((G^0_n)_{2n+2}\) for correlation energies in Eq. (5). In the following context, we provide a different derivation, which is more explicit and unveils the underlying fundamental moment-cumulant relation. More importantly, in this way we are able to write down an explicit expression for det \((G^0_{2n+2})_{n}\) in terms of principal minors of det \((G^0_{2n+2})_{n}\).

Let us first consider the explicit formula for a determinant det \((A_n)_{n}\) of an \(n\)-by-\(n\) matrix \(A_n\),

\[
det(A_n) = \sum_{g \in S_n} \text{sgn}(g) A_{1,g(1)} \cdots A_{n,g(n)},
\]

where the summation is over all permutations \(g \in S_n\) and sgn\((g)\) is the signature of the permutation \(g\). For each permutation, we apply the cycle decomposition, e.g.,

\[
g_a = (13)(5)(2)(46) = (13)(5)(2)(46).
\]

Some typical examples are shown in Fig. 1 for \(n = 6\). Since the signature sgn\((g)\) can also be decomposed, e.g., sgn\((g_a)\) = sgn\((135)\) = sgn\((2)\) = sgn\((46)\) = \((-1)^{(135)}(-1)^{(2)}(-1)^{(46)}\) = 1\(^{13}\), where \(|(135)| = 3\) represents the length of the cycle \((135)\), diagrammatically, we are able to rewrite each term in Eq. (8) as a product of loops, see Fig. 1. For example, the term for \(g_a\) can be written compactly as \(l((135)(2)(46)\), where the loop product \(l(i_1i_2\cdots i_k) \equiv (-1)^{k-1} A_{i_1,i_2} \cdots A_{i_{k-1},i_k} A_{i_k,i_1}\) for each cycle \((i_1i_2\cdots i_k)\). Then, the sum over \(n!\) permutations in Eq. (8) can be greatly simplified, by realizing that the sum over all the terms corresponding to the same set partition can be simplified into a single product, e.g., \(l((135)+(153))(2)(46)\) for permutations \(g_a\) and \(g_b\) (see Fig. 1) generated from the set partition \(\pi = \{\{1,3,5\},\{2\},\{4,6\}\}\). Thus, through this construction, in general, we can express a determinant as a sum over partitions, where each partition contributes to a single product.

**Theorem 2** (loop expansion of determinants). Given an elementary index set \(\mathcal{I} = \{1,\cdots,n\}\), Eq. (8) can be
where $\pi$ represents a set partition of with length $|\pi|$, viz., $\pi = \{I_1, I_2, \ldots, I_{|\pi|}\}$ with the $k$-th block $I_k = \{i_1, i_2, \ldots, i_{|I_k|}\}$, and $\kappa(I_k)$ is a sum over contributions from the $|I_k| - 1)!$ possible cycles generated from the index set $I_k$, with $l_i(I_k)$ being the loop contribution from one of the cycles.

In a Feynman (Goldstone) diagrammatic language, Eq. (10) is nothing but a mathematical description of the fact that loops formed by Green’s functions are building block for all diagrams, as highlighted by different colors in Fig. 1 for selected third-order diagrams. Furthermore, the quantity $\kappa(I_k)$ sums over all possible loops generated from the points in $I_k$. If one-body operators are considered as the only perturbations, then $\kappa(I)$ is simply the sum over all connected diagrams, because in this case the definition of connectivity with respect to perturbations coincides with the graphical definition. For many-body perturbations, different loops can be glued together by interaction lines to form a connected diagrams, as shown in Fig. 1. In such case, we can redefine the index set, e.g., $\mathcal{I} = \{\nu_0, \ldots, \nu_n\}$ for det($G^0_{2n+2}$) in our case, with each element corresponding to one interaction pair (i.e., two points in graph). Then, exactly the same relation (10) holds for $\mathcal{I}$, because terms like $\kappa(\{1,2,3,4\})$ and $\kappa(\{1\}, \{2,3,4\})$ defined in the elementary index set $\{1,2,3,4\}$ will be summed to $\kappa(\{1,2\}, \{3,4\})$ defined for the coarser index set $\{1,2\}, \{3,4\}$. The importance of Eq. (10) lies in that it is the same as the moment-cumulant relation in the multivariate case, such that the inversion of this relation is known. Therefore, summarizing these results, we have the following explicit expression for det$_c(G^0_{2n+2})$.

**Theorem 3** (moment-cumulant relation). Let $\mathcal{I} = \{\nu_0, \ldots, \nu_n\}$, the moments defined as $\mu(\mathcal{I}) \triangleq \text{det}(G^0_{2n+2})$, and other $\mu(I_k)$ being the principal minors of det($G^0_{2n+2}$) with both columns and rows constructed from $I_k$, the cumulant $\kappa(\mathcal{I}) \triangleq \text{det}_c(G^0_{2n+2})$ is given explicitly as

$$\kappa(\mathcal{I}) = \sum_\pi (|\pi| - 1)!(-1)^{|\pi| - 1} \prod_{I_k \in \pi} \mu(I_k),$$

which can be viewed as an inversion of the relation (10) in the particular setting.

The coefficient $(|\pi| - 1)!$ is nontrivial in the sense that it is a reflection of the nontrivial symmetric factor in diagrams for energy/energy, which is more complicated than that in diagrams for Green’s functions (which would be simply one). The connection to the moment-cumulant relation is physically quite appealing, since it is a reflection of the linked cluster theorem, and ensures that the correlation energy at each order is size-extensive.

The number of partitions in the sum (11) is given by the Bell number $B_n$, which are $B_2 = 2$, $B_3 = 5$, $B_4 = 15$, and $B_5 = 52$ for the lowest few orders, and it growth, bound by $(0.792n/ln(n+1))^{43}$ is much slower than factorial. With the HF reference as in our case, Eq. (11) can be further simplified, since the effect of the term $-V_{HF}$ in $V$ is equivalent to set the diagonal 2-by-2 blocks of $G^0_{2n+2}$ be zero, such that $\kappa(\{\nu_i\}) = 0$. Consequently, the lowest few orders can be expressed compactly as

$$\kappa^{\text{MP2}} = \mu(\{\nu_0, \nu_1\}) \triangleq \mu_{01}, \quad (12)$$

$$\kappa^{\text{MP3}} = \mu(\{\nu_0, \nu_1, \nu_2\}) \triangleq \mu_{012}, \quad (13)$$

both of which just involve a single determinant. On the right hand sides, to make notations simpler, we have introduced a shorthand notation. Likewise, $\kappa$ for MP4 and MP5 can be written compactly as

$$\kappa^{\text{MP4}} = \mu_{0123} - \mu_{01\mu_{23}} - \mu_{02\mu_{13}} - \mu_{03\mu_{12}} \quad (14)$$

$$\kappa^{\text{MP5}} = \mu_{01234} - \mu_{012\mu_{34}} - \mu_{013\mu_{24}} - \mu_{014\mu_{23}} - \mu_{023\mu_{14}} - \mu_{024\mu_{13}} - \mu_{034\mu_{12}} - \mu_{01\mu_{234}} - \mu_{02\mu_{134}} - \mu_{03\mu_{124}} - \mu_{04\mu_{123}}. \quad (15)$$

These expressions are remarkably simpler than the integrands based on the sum of individual Goldstone diagrams.

In general, the cost of Eq. (11) is $O(2^n n^3)$ for computing all the moments $\mu$ involved from principal minors of $G^0_{2n+2}$, and $O(n B_n)$ for assembling $\kappa_{n+1}$ from Eq. (11), estimated by the number of multiplications. Thus, the use of the determinant trick to sum diagrams, which is a common technique in fermionic QMC for lattice models [10], is essential to avoid the factorial complexity of diagrams at high orders. For $n \geq 6$, Eq. (11) starts to contain common intermediates shared by different set partitions, e.g., $-\mu_{0123\mu_{45}} + \mu_{01\mu_{23}\mu_{45}} - (\mu_{0123} - \mu_{01\mu_{23}})\mu_{45}$. Then, the recursive algorithm [13] becomes more advantageous. Having identified the moment-cumulant relation for $\mu$ and $\kappa$, the recursive formula can be readily derived by translating the recursive relation [13] between multivariate moments and cumulants directly,

$$\kappa(\mathcal{I}) = \mu(\mathcal{I}) - \sum_{S \subseteq \mathcal{I}, S \neq \emptyset} \kappa(\{\nu_0\} \cup S) \mu(\mathcal{I} \setminus S), \quad (16)$$

where $\mathcal{I} \triangleq \mathcal{I} \setminus \{\nu_0\}$, and $S \neq \emptyset$ comes from the choice of HF reference. This can reduce the cost for assembling $\kappa_{n+1}$ to $O(3^n)$ asymptotically [13].

**V. MONTE CARLO ALGORITHM AND ILLUSTRATIVE EXAMPLE**

After established the formula for MP$n$ correlation energies [4], we now consider its evaluations. The dimensionality of integrations for each $\nu$ in Eq. (11) is
of the system. In this work, we investigated two choices
where \( \Delta = \varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}} \) is the zeroth-order HF gap of the system. Specifically, at or-
ping \( n+1 \), we define an importance sampling function
\[ p(nK + 1|v_0, \cdots, v_n) = \prod_{k=0}^{n} p(v_k) \] for the configuration \( nK + 1 = \{v_0, \cdots, v_n\} \),
\[
p(v_k) = p(\tau_k)p(\sigma_k)p(\sigma'_k)p(\bar{\tau}_k, \bar{\tau}'_k),
\]
\[
p(\tau_k) = \Delta^{\Delta^\tau}, \quad \tau \in (-\infty, 0),
\]
\[
p(\sigma_k) = \frac{1}{2}, \quad \sigma \in \{\alpha, \beta\},
\] (17)
where \( \Delta = \varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}} \) is the zeroth-order HF gap of the system. In this work, we investigated two choices for \( p(\bar{\tau}_k, \bar{\tau}'_k) \),
\[
p_A(\bar{\tau}_k, \bar{\tau}'_k) = p(\bar{\tau}_k)p(\bar{\tau}'_k),
\]
\[
p_B(\bar{\tau}_k, \bar{\tau}'_k) = \frac{1}{E_{\tau}} |\bar{\tau}_k - \bar{\tau}'_k| p(\bar{\tau}_k)p(\bar{\tau}'_k),
\] (18)
(19)
where \( p(\bar{\tau}) = \frac{1}{K} \sum_{k=1}^{K} |\psi_k(\bar{\tau})|^2 \), \( K \) is the dimensionality of molecular orbitals (MO), and \( E_{\tau} \) is a normalization factor. Note that for \( v_0 \), there is no need to generate \( \tau_0 \). The two electrons within the same pair are generated via the standard Markov Chain Monte Carlo (MCMC) method. Eq. (18) is then evaluated simply from the average \( \frac{(-1)^n}{2^{n+1}} \frac{p(nK + 1|v_0, \cdots, v_n)}{p(nK + 1)} \). The entire algorithm is summarized in Fig. 2.

The expensive steps in each Monte Carlo step include: \( O(nK) \) for evaluating the values of atomic orbitals (AO) at the sampled spatial points and \( O(nK^2) \) for transformation from AO to MO in step 2 (line 7 in Fig. 2), \( O(n^2K) \) for constructing \( G_{2n+2}^0 \) in step 3 (line 10), and \( O(f(n)) \) for evaluating \( \kappa_{n+1} \) in step 4 (line 11), where \( f(n) \) is a function depending on a specific numerical scheme (Eq. (11) or (16)) for \( \kappa_{n+1} \). Thus, the total computational cost scales as \( O(nK^2 + n^2K + f(n)) \). For large systems, assuming \( K \) is proportional to the system size \( N \), the present algorithm scales as \( O(N^2) \) asymptotically.

To examine the correctness of our formulation in the above sections, we have implemented the above algorithm in Fig. 2 in an in-house program package SMBPT, and studied the prototypical molecule \( \text{H}_2 \) with STO-3G at the equilibrium geometry \( R_{\text{H-H}} = R_e = 0.74144A \) and a stretched geometry \( R_{\text{H-H}}=4A \) with Eqs. (18) (scheme A) and (19) (scheme B). Albeit being trivial for traditional quantum chemistry methods, this problem is nontrivial and considerably more complicated than the corresponding two-site Hubbard model for QMC due to the use of a realistic Coulomb interaction in real space. The data obtained with sample size being \( 10^6 \) are shown in Table I. Overall, we found the MPn series can be reproduced by the present stochastic scheme at both geometries. Using the summation based on momentum-cumulant relations, it successfully extends the previous MC methods \(^{10,11}\) for MP2 and MP3 to higher orders with a reasonable computational cost. It can be seen that the scheme B leads to slightly more accurate results than the scheme A.

\[
\begin{array}{ccc}
\hline
n & \text{exact} & \text{scheme A} \ (18) & \text{scheme B} \ (19) \\
\hline
1 & -0.67448 \pm 0.00005 & -0.67450 \pm 0.00004 \\
2 & -0.01317 \pm 0.00001 & -0.01317 \pm 0.00001 \\
3 & -0.00485 \pm 0.00000 & -0.00485 \pm 0.00000 \\
4 & -0.00172 \pm 0.00000 & -0.00172 \pm 0.00000 \\
5 & -0.00058 \pm 0.00000 & -0.00058 \pm 0.00000 \\
6 & -0.00019 \pm 0.00000 & -0.00022 \pm 0.00008 \\
\hline
\end{array}
\]

\[
\begin{array}{c}
\text{Table I. Computed MPn energies } E_n \text{ for H}_2 \text{ with STO-3G at the equilibrium geometry } R_{\text{H-H}} = R_e \text{ and a stretched geometry } R_{\text{H-H}}=4A \text{ using two different importance sampling functions (scheme A with (18) and scheme B with (19)). The sample size is } N_{\text{MC}} = 10^6. \\
\end{array}
\]

At higher orders, a new difficulty is found in stochastic evaluations of the MPn series, which is not obvious in the study of low orders. From Table I, we observed a rapid growth of variance as \( n \) increases, in particular at the stretched geometry, where the interaction becomes stronger. This is likely due to both the simplicity of our importance sampling functions as well as the fermionic sign problem, since \( \kappa \) is not always positive. Therefore, while the obtained data are overall quite encouraging, further investigations are necessary to fully understand the exact origin of such problem. Along with other possible improvements, e.g., faster algorithms for computing \( \mu \) and assembling \( \kappa \), alternative definitions for \( \kappa \), as well as improved sampling techniques, this will be the subject of a subsequent study.

VI. SUMMARY

In summary, we presented a reformulation of standard MBPT for correlation energies into a general form \(^4\) using Theorems \(^4\) and \(^5\), which involves multidimensional integrations that can be evaluated by Monte Carlo algorithms. The proposed QMC algorithm share similarities with MC-MP2 and MC-MP3\(^{10,11}\), such as its low formal scaling \( O(N^2) \), which makes it promising for large systems. The major differences are twofold. First, we use an efficient algorithm based on momentum-cumulant relations, which avoids the factorial scaling in using Goldstone diagrams. Second, in our algorithm all the spatial, spin, and imaginary time variables are sampled stochastically, which are necessary ingredients for high-order perturbation theories. Like FCIQMC\(^{13}\) (full configuration interaction quantum Monte Carlo) and AFQMC\(^{14}\) (auxiliary field QMC), the present QMC algorithm is formulated within an orbital space, but its evaluation in real space is more similar to standard VMC (variational MC) and DMC. The advantage of the real-space evaluation is its lower computational scaling.
and lower requirement for storage with respect to the system size. However, if full molecular integrals are affordable, as for small systems, it is also possible to adapt the present QMC algorithm to the sampling based on molecular integrals as in FCIQMC. Apart from correlation energies, several other extensions can be readily envisaged, such as the extension to the finite temperature case and physical properties other than energies. From a practical aspect, there are still a few obstacles to be overcome in future. Most importantly, improved sampling methods, along with with ways to alleviate the fermionic sign problem, need to be developed in order to apply the stochastic MBPT to large basis sets and systems. Investigations along these lines are being carried out in our laboratory.

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