

Stochastic evaluation of second-order many-body perturbation energies

Soohaeng Yoo Willow, Kwang S. Kim, and So Hirata'

Citation: *J. Chem. Phys.* **137**, 204122 (2012); doi: 10.1063/1.4768697

View online: <http://dx.doi.org/10.1063/1.4768697>

View Table of Contents: <http://aip.scitation.org/toc/jcp/137/20>

Published by the [American Institute of Physics](#)

COMPLETELY

REDESIGNED!



**PHYSICS
TODAY**

Physics Today Buyer's Guide
Search with a purpose.

Stochastic evaluation of second-order many-body perturbation energies

Soohaeng Yoo Willow,^{1,2} Kwang S. Kim,² and So Hirata^{1,a)}¹Department of Chemistry, University of Illinois at Urbana-Champaign, 600 South Mathews Avenue, Urbana, Illinois 61801, USA²Center for Superfunctional Materials, Department of Chemistry, Pohang University of Science and Technology, San 31, Hyojadong, Namgu, Pohang 790-784, South Korea

(Received 21 September 2012; accepted 8 November 2012; published online 29 November 2012)

With the aid of the Laplace transform, the canonical expression of the second-order many-body perturbation correction to an electronic energy is converted into the sum of two 13-dimensional integrals, the 12-dimensional parts of which are evaluated by Monte Carlo integration. Weight functions are identified that are analytically normalizable, are finite and non-negative everywhere, and share the same singularities as the integrands. They thus generate appropriate distributions of four-electron walkers via the Metropolis algorithm, yielding correlation energies of small molecules within a few mE_h of the correct values after 10^8 Monte Carlo steps. This algorithm does away with the integral transformation as the hotspot of the usual algorithms, has a far superior size dependence of cost, does not suffer from the sign problem of some quantum Monte Carlo methods, and potentially easily parallelizable and extensible to other more complex electron-correlation theories. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4768697>]

I. INTRODUCTION

The second-order many-body perturbation correction¹ to the Hartree–Fock (HF) energy of a molecule is

$$E^{(2)} = E_A^{(2)} + E_B^{(2)}, \quad (1)$$

with

$$E_A^{(2)} = 2 \sum_{i,j}^{\text{occ.}} \sum_{a,b}^{\text{vir.}} \frac{\langle ij|ab\rangle \langle ab|ij\rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}, \quad (2)$$

$$E_B^{(2)} = - \sum_{i,j}^{\text{occ.}} \sum_{a,b}^{\text{vir.}} \frac{\langle ij|ab\rangle \langle ab|ji\rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}, \quad (3)$$

where $\langle ij|ab\rangle$ is a two-electron integral defined below, ϵ_i is the canonical HF orbital energy of the i th orbital, and the summations must be taken over all occupied (labeled by i and j) and all virtual (a and b) orbitals. The Møller–Plesset partitioning of the Hamiltonian is assumed. This theory, MP2 or MBPT(2), accounts for the majority of the correlation energy. It is also the simplest member of the systematic series of approximations formally convergent to the exact eigenvalue of the Schrödinger equation and thus holds special importance in *ab initio* molecular orbital (MO) theory.

The two-electron integrals appearing in the above expressions are 6-dimensional and involve four MO's,

$$\langle pq|rs\rangle = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \frac{\varphi_p^*(\mathbf{r}_1)\varphi_q^*(\mathbf{r}_2)\varphi_r(\mathbf{r}_1)\varphi_s(\mathbf{r}_2)}{r_{12}}, \quad (4)$$

where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. The MO's, $\{\varphi_p\}$, are, in turn, related to atomic-orbital (AO) basis functions, $\{\chi_\kappa\}$, by

$$\varphi_p(\mathbf{r}) = \sum_{\kappa} C_p^{\kappa} \chi_{\kappa}(\mathbf{r}). \quad (5)$$

^{a)}sohirata@illinois.edu.

The expansion coefficients, $\{C_p^{\kappa}\}$, are a part of the solution of the HF problem and should be available prior to the MP2 procedure. The two-electron integrals over the MO's are, therefore, obtained by transforming those over AO's, which are defined elsewhere,¹

$$\langle pq|rs\rangle = \sum_{\kappa,\lambda,\mu,\nu} C_p^{\kappa*} C_q^{\lambda*} C_r^{\mu} C_s^{\nu} \langle \kappa\lambda|\mu\nu\rangle. \quad (6)$$

The number of arithmetic operations in this step increases as the fifth power of the number of MO's. This transformation—not the evaluation of Eq. (2) or (3)—constitutes the computational bottleneck of the whole MP2 calculation. It also tends to be the hardest part to program into an efficient, parallel-scalable code because of the large number of data involved and disparate nature of the AO's and MO's.

Can one bypass the integral transformation and, ultimately, contrive an algorithm of MP2 that has more manageable, i.e., less steep, size dependence of cost? Can the algorithm be simpler and thus straightforwardly extended to more complex theories and more easily parallelized? In this article, we propose such an algorithm that combines Almlöf's Laplace-transform expression of MP2 energy² and Monte Carlo (MC) integration³ of the 12-dimensional parts of the resulting 13-dimensional functions. The details are described below.

II. THEORY

Equations (2) and (3) involve the denominator, $\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b$, which makes the summations over all four orbitals (i , j , a , and b) coupled. However, using the Laplace transform,²

$$\frac{1}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} = - \int_0^{\infty} d\tau \exp\{(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)\tau\}, \quad (7)$$

one can interchange the order of summations and integrations and obtain the following alternative expressions wherein the summations over orbitals are now decoupled:

$$E_A^{(2)} = -2 \int d\mathbf{r}_1 \int d\mathbf{r}_2 \int d\mathbf{r}_3 \int d\mathbf{r}_4 \int_0^\infty d\tau \frac{o(\mathbf{r}_1, \mathbf{r}_3, \tau) o(\mathbf{r}_2, \mathbf{r}_4, \tau) v(\mathbf{r}_1, \mathbf{r}_3, \tau) v(\mathbf{r}_2, \mathbf{r}_4, \tau)}{r_{12} r_{34}}, \quad (8)$$

$$E_B^{(2)} = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \int d\mathbf{r}_3 \int d\mathbf{r}_4 \int_0^\infty d\tau \frac{o(\mathbf{r}_1, \mathbf{r}_3, \tau) o(\mathbf{r}_2, \mathbf{r}_4, \tau) v(\mathbf{r}_1, \mathbf{r}_4, \tau) v(\mathbf{r}_2, \mathbf{r}_3, \tau)}{r_{12} r_{34}}, \quad (9)$$

with

$$o(\mathbf{r}_1, \mathbf{r}_3, \tau) = \sum_i^{\text{occ.}} \varphi_i^*(\mathbf{r}_1) \varphi_i(\mathbf{r}_3) \exp(\epsilon_i \tau), \quad (10)$$

$$v(\mathbf{r}_1, \mathbf{r}_3, \tau) = \sum_a^{\text{vir.}} \varphi_a(\mathbf{r}_1) \varphi_a^*(\mathbf{r}_3) \exp(-\epsilon_a \tau). \quad (11)$$

Equations (8) and (9) are both 13-dimensional integrals of slightly more involved integrands. They may be ideally evaluated by MC, whose statistical errors are known to decrease as the inverse square root of the number of sampling points regardless of dimensionality. They can be contrasted with the original expressions, Eqs. (2) and (3), which are the sums of enormous numbers of lower-dimensional integrals, which may be evaluated efficiently by recursion formulas,⁴ but need to be stored and transformed. Here, we apply MC integrations to the 12 dimensions spanned by \mathbf{r}_1 , \mathbf{r}_2 , \mathbf{r}_3 , and \mathbf{r}_4 in Eqs. (8) and (9), while the integration over τ is carried out more suitably by a quadrature (see below).

Generally, a MC integration³ approximates an integral of a high-dimensional function, $f(\mathbf{x})$, by the summation of the quotient $f(\mathbf{x}_n)/w(\mathbf{x}_n)$ evaluated at increasingly many random sampling points, $\{\mathbf{x}_n\}$, distributed according to the weight function, $w(\mathbf{x})$:

$$I = \int d\mathbf{x} f(\mathbf{x}), \quad (12)$$

$$= \int d\mathbf{x} \frac{f(\mathbf{x})}{w(\mathbf{x})} w(\mathbf{x}), \quad (13)$$

$$\approx \frac{1}{N} \sum_{n=1}^N \frac{f(\mathbf{x}_n)}{w(\mathbf{x}_n)}, \quad (14)$$

where N is the number of MC steps or sampling points. The proper choice of the weight function is crucial for the efficiency or even the viability of MC integration; $w(\mathbf{x})$ should be as close as possible to $|f(\mathbf{x})/I|$ so that the quotient $f(\mathbf{x})/w(\mathbf{x})$ is smooth and thus integrated easily with fewer sampling points.

Thanks to the Metropolis–Rosenbluth–Rosenbluth–Teller–Teller algorithm (hereafter simply the Metropolis algorithm),⁵ we now can generate a distribution of sampling points according to a variety of forms of $w(\mathbf{x})$. Nevertheless, we must still impose certain conditions on the form such as

$$w(\mathbf{x}) \geq 0, \quad (15)$$

$$\int d\mathbf{x} w(\mathbf{x}) = 1, \quad (16)$$

and, furthermore,

$$\left| \frac{f(\mathbf{x})}{w(\mathbf{x})} \right| < \infty, \quad (17)$$

except at a countable number of points.³ In our context, since the integrands in Eqs. (8) and (9) are singular at $r_{12} = 0$ and $r_{34} = 0$, we must require $w(\mathbf{x})$ to have the same singularities at the same positions and, generally, behaves like $f(\mathbf{x})$ elsewhere.

Here, we propose the following weight function that satisfies all these conditions:

$$w_\rho(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) = \frac{1}{E_J^2} \frac{\rho(\mathbf{r}_1) \rho(\mathbf{r}_2) \rho(\mathbf{r}_3) \rho(\mathbf{r}_4)}{r_{12} r_{34}}, \quad (18)$$

where $\rho(\mathbf{r})$ is the electron density of the molecule,

$$\rho(\mathbf{r}) = 2 \sum_i^{\text{occ.}} \varphi_i^*(\mathbf{r}) \varphi_i(\mathbf{r}), \quad (19)$$

and E_J is the so-called Coulomb energy of the HF theory given by

$$E_J = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \frac{\rho(\mathbf{r}_1) \rho(\mathbf{r}_2)}{r_{12}}. \quad (20)$$

The value of E_J should be known from the preceding HF calculation. It is straightforward to verify that w_ρ satisfies Eqs. (15)–(17), and has the same $(r_{12} r_{34})^{-1}$ singularity as the integrands of Eqs. (8) and (9).

Numerically, however, the quotients in Eq. (14) can become quite large where the density is vanishingly small and the virtual orbitals in the integrands are diffuse. We, therefore, consider the following weight function also:

$$w_g(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) = \frac{1}{E_g^2} \frac{g(\mathbf{r}_1) g(\mathbf{r}_2) g(\mathbf{r}_3) g(\mathbf{r}_4)}{r_{12} r_{34}}, \quad (21)$$

where $g(\mathbf{r})$ is, typically, but not necessarily, a sum of s -type Gaussian functions centered at atoms and

$$E_g = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \frac{g(\mathbf{r}_1) g(\mathbf{r}_2)}{r_{12}}, \quad (22)$$

which can be evaluated analytically.⁴ The prefactors and exponents of the Gaussian functions are adjusted so as to maximize the sampling efficiency.

The proposed algorithm of the Monte Carlo MP2 (MC-MP2) can thus be outlined as follows. A *walker* explores the 12-dimensional space of four electrons (\mathbf{r}_1 through \mathbf{r}_4). These electron coordinates are distributed according to the weight function w_ρ or w_g by the Metropolis algorithm. For a given set of electron coordinates accepted by the Metropolis test, we evaluate the orbitals and then the integrands of Eqs. (8)

and (9) at a fixed value of τ . We also evaluate the value of the weight function at the same set of coordinates. The MP2 energy is updated with the contribution from this walker position using Eq. (14). The integration over τ is carried out with a quadrature since this dimension is essentially decoupled from the rest. We thus employ the Gauss–Kronrod quadrature⁶ after the following conversion of the integration variable is made:

$$\int_0^\infty d\tau \exp\{(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)\tau\} \\ = \int_0^1 \frac{d\tilde{\tau}}{\tilde{\tau}^2} \exp\{(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)(1 - \tilde{\tau})/\tilde{\tau}\}. \quad (23)$$

The statistical uncertainty, ε , of the integral is computed by

$$\varepsilon^2 = \frac{1}{N} \text{var} \left(\frac{f(\mathbf{x})}{w(\mathbf{x})} \right), \quad (24)$$

$$\text{var} \left(\frac{f(\mathbf{x})}{w(\mathbf{x})} \right) = \frac{1}{N-1} \sum_{n=1}^N \left\{ \frac{f(\mathbf{x}_n)}{w(\mathbf{x}_n)} - I \right\}^2, \quad (25)$$

where $\text{var}(\mathbf{x})$ is the variance of a random variable \mathbf{x} and I is given by Eq. (14). This simple expression is, however, said to underestimate the true uncertainty because the autocorrelation time is ignored. Flyvbjerg and Petersen suggested the more accurate procedure known as the blocking method.⁷ This method transforms the original data set $\{\mathbf{x}_1, \dots, \mathbf{x}_N\}$ into the new data set $\{\mathbf{x}'_1, \dots, \mathbf{x}'_{N/m}\}$ by “blocking” of m data as

$$\mathbf{x}'_i = \frac{1}{m} \{\mathbf{x}_{m(i-1)+1} + \dots + \mathbf{x}_{mi}\} \quad (26)$$

and defines the uncertainty, ε' , using the variance of these blocked data. The uncertainty of the blocked data, ε' , is higher and more accurate than ε . In this study, we employed $m = 5$.

The advantages of the proposed new algorithm of MC-MP2 over the conventional one are the following. First, the polynomial dependence of the cost per MC step is only quadratic with respect to the numbers of MO's and AO's (see below) as opposed to quintic dependence of the conventional MP2 algorithm. Second, MC allows the importance sampling in high dimensions, which is next to impossible with cubature where one is almost always limited to using a “product” grid, which has optimal distributions of grid points only along each dimension, but not in the whole high dimension. Third, the algorithm is naturally parallel as it consists in the completely independent evaluations of integrands at random sampling points carried out concurrently, in any order, and even allowed to fail without crashing the entire calculation. Fourth, the algorithm is so simple that it can likely be extended to more complex or higher-dimensional methods such as third-order and higher-order many-body perturbation theories,¹ applications to solids,⁸ quasiparticle energies,⁸ correlation corrections to excitation energies,^{9,10} explicitly correlated methods,^{11,12} etc. The primary disadvantages are the inevitable statistical errors and also a large prefactor multiplying the polynomial dependence of the cost.

While sharing the similar goal, our MC-MP2 method fundamentally differs from “stochastic perturbation theory” proposed by Thom and Alavi¹³ (see also Refs. 14–16). The difference is that, in their method, walkers explore the high-dimensional Hilbert space with the assumption that the two-electron integrals over MO's are readily available, while, in MC-MP2, a walker represents four electrons roaming in real space and neither the integral transformation nor the two-electron integrals over MO's is necessary.

Our MC-MP2 and the (phaseless) auxiliary-field quantum Monte Carlo (AFQMC)^{17–19} both combine established electronic structure methods and even software with MC integration, but otherwise they have few features in common. In AFQMC, a one-electron theory with an auxiliary field is a computational intermediate to solve the Schrödinger equation within a finite basis set and suffers from the so-called sign problem unless the phaseless approximation¹⁹ is used. MC-MP2 aims at obtaining finite-basis-set MP2 energies and the only errors it incurs are statistical ones.

Among the various incarnations of quantum Monte Carlo (QMC) methods,^{3,20–23} MC-MP2 may be most similar to variational MC (VMC). The difference is, of course, that the latter is variational and needs to optimize some parameters, whereas MC-MP2 has no parameters to optimize and is not variational. The VMC, however, has the great advantage of being a zero-variance method, which MC-MP2 is not. MC-MP2 may, on the other hand, be extensible to (non-variational) properties other than ground-state energies (e.g., quasiparticle energies) that may be more difficult to obtain with VMC.

III. RESULTS AND DISCUSSION

Table I compiles the MP2 correlation energies of the N₂ and O₂ molecules obtained by MC and conventional algorithms. Figure 1 shows the convergence of the energies and uncertainties for N₂ as a function of the MC steps. In both, the MC results obtained with two types of weight functions are shown. The form of $g(\mathbf{r})$ in w_g used in our study is

$$g(\mathbf{r}) = \sum_{m=1}^2 \left\{ \exp(-\zeta_1 r_m^2) + c \exp(-\zeta_2 r_m^2) \right\}, \quad (27)$$

with $\zeta_1 = 0.6$, $\zeta_2 = 0.1$, and $c = 0.01$ for N₂ and $\zeta_1 = 0.7$, $\zeta_2 = 0.2$, and $c = 0.01$ for O₂, where r_m denotes the distance from the m th atom.

TABLE I. The MP2/6-31G** (frozen core) correlation energies and uncertainties (both in E_h) of N₂ (1.42 Å) and O₂ (1.20 Å) obtained with the conventional and MC methods.

Molecule	Method	$E^{(2)}$	ε	ε'
N ₂	Conventional	-0.4373
N ₂	MC ($N = 10^8$; w_ρ)	-0.4391	0.0080	0.0156
N ₂	MC ($N = 10^8$; w_g)	-0.4396	0.0037	0.0053
O ₂	Conventional	-0.3636
O ₂	MC ($N = 10^8$; w_ρ)	-0.3682	0.0091	0.0175
O ₂	MC ($N = 10^8$; w_g)	-0.3649	0.0045	0.0065

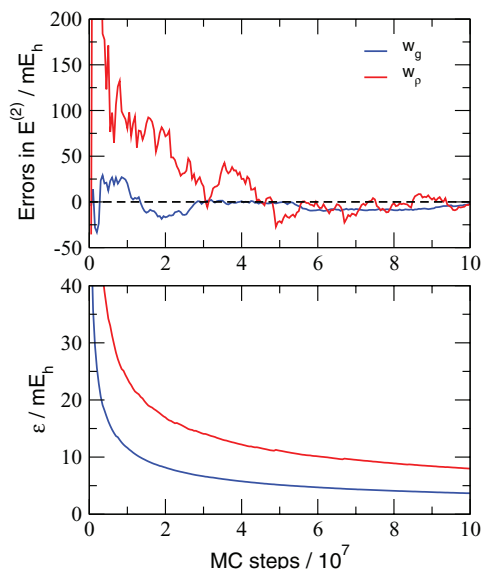


FIG. 1. The errors in the MC-MP2/6-31G** (frozen core) correlation energies of N_2 (1.42 Å) and the uncertainties (both in mE_h) as a function of the MC steps.

The MC algorithm is capable of reproducing the correct MP2 energies after 10^8 steps within a few mE_h either with w_ρ or w_g . The corresponding uncertainties are consistent with the errors and are on the order of several mE_h . Figure 1 shows the rugged convergence of energies and the smooth $N^{-1/2}$ convergence of the uncertainties. The uncertainty ε' from the blocking method⁷ is higher than ε by a factor of 1.5 to 2. The plot for O_2 is very similar.

Clearly, w_g offers greater efficiency than w_ρ . We ascribe this to the more diffuse nature of w_g than w_ρ and hence to the fact that walkers can explore a greater space with w_g . In other words, w_ρ may have too large weights around the atomic core regions. For instance, the smallest exponent of the Gaussian function in the O 6-31G** basis set is 0.270058, while we chose the exponent of 0.2 in w_g . In all cases considered, the fine-tuning of exponents in w_g leads to a reduction in ε' or ε by a factor of two relative to w_ρ .

Table II lists the results of the conventional and MC-MP2 calculations of water clusters, $(H_2O)_n$, with $n = 1, 2$, and 3.

TABLE II. The MP2/6-31G** (frozen core) correlation energies and uncertainties (both in E_h) of $(H_2O)_n$ ($n = 1, 2$, and 3) obtained with the conventional and MC methods. The central processing unit (CPU) time (in seconds) are also given.

Molecule	Method	$E^{(2)}$	ε	ε'	CPU
H_2O	Conventional	-0.1970	0.4
H_2O	MC ($N = 10^8$; w_ρ)	-0.1974	0.0051	0.0099	3.4×10^3
H_2O	MC ($N = 10^8$; w_g)	-0.1940	0.0028	0.0040	2.5×10^3
$(H_2O)_2$	Conventional	-0.3966	20.1
$(H_2O)_2$	MC ($N = 2 \times 10^8$; w_ρ)	-0.3749	0.0135	0.0250	32×10^3
$(H_2O)_2$	MC ($N = 2 \times 10^8$; w_g)	-0.3872	0.0079	0.0112	22×10^3
$(H_2O)_3$	Conventional	-0.6014	163
$(H_2O)_3$	MC ($N = 3 \times 10^8$; w_ρ)	-0.6445	0.0238	0.0462	13×10^4
$(H_2O)_3$	MC ($N = 3 \times 10^8$; w_g)	-0.6178	0.0161	0.0232	86×10^3

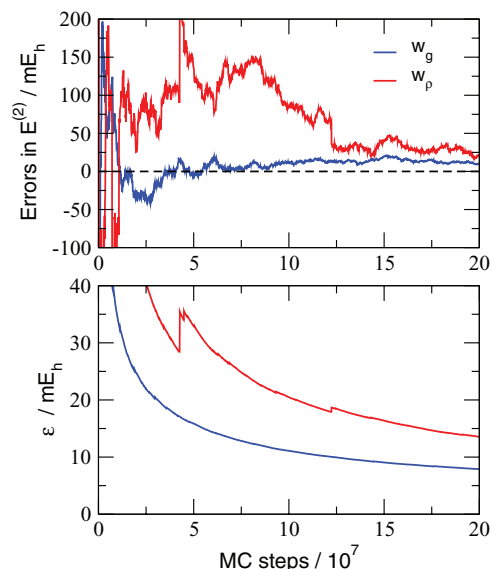


FIG. 2. The errors in the MC-MP2/6-31G** (frozen core) correlation energies of $(H_2O)_2$ and the uncertainties (both in mE_h) as a function of the MC steps.

For $g(\mathbf{r})$ in w_g , we used

$$g(\mathbf{r}) = \sum_{o=1}^n \{ \exp(-\zeta_1 r_o^2) + c_1 \exp(-\zeta_2 r_o^2) \} + c_3 \sum_{h=1}^{2n} \{ \exp(-\zeta_3 r_h^2) + c_2 \exp(-\zeta_4 r_h^2) \}, \quad (28)$$

where r_o and r_h refer to the distances from the o th oxygen and h th hydrogen atom, respectively, and $\zeta_1 = 0.7$, $\zeta_2 = 0.15$, $\zeta_3 = 0.5$, $\zeta_4 = 0.1$, $c_1 = 0.1$, $c_2 = 0.1$, and $c_3 = 0.16$. The smallest exponent for each atom was chosen to be smaller than the smallest exponent in the corresponding atom's 6-31G** basis functions.

The errors in the MP2 energies obtained with w_ρ are a few tens of mE_h , while those with w_g tend to be smaller. Figure 2 compares the convergence of the results obtained with w_g and w_ρ for $(H_2O)_2$. Again, the lower efficiency of w_ρ is due to the larger quotients $|f(\mathbf{x})/w(\mathbf{x})|$ where the electron density is vanishingly small, but some virtual orbitals are not. To confirm the convergence, we have performed longer calculations up to 8×10^8 MC steps. In Fig. 3, the convergence within several mE_h of the conventional results can be seen for all of $(H_2O)_n$ ($n = 1, 2$, and 3).

For clusters of n non-interacting molecules, the variance and uncertainty should increase as n and $n^{1/2}$, respectively, because

$$\text{var} \left(\frac{nf(\mathbf{x})}{w(\mathbf{x})} \right) = n \text{var} \left(\frac{f(\mathbf{x})}{w(\mathbf{x})} \right). \quad (29)$$

Hence, when nN MC steps for the n non-interacting molecules are taken (as done in Table II albeit for interacting water molecules), the uncertainty should become the same as the uncertainty for the monomer with N MC steps in view of the $N^{-1/2}$ falloff of the uncertainty.

The data in Table II indicate that this expected behavior is not observed and the uncertainty grows with the number of

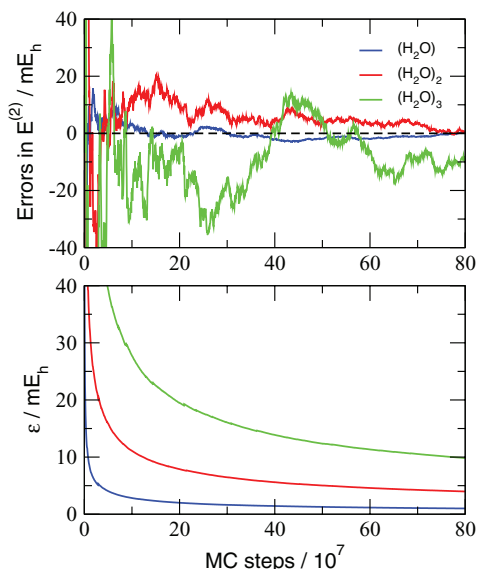


FIG. 3. The same as Fig. 2 for $(\text{H}_2\text{O})_n$ ($n = 1, 2,$ and 3) with w_g .

interacting water molecules despite the proportional increase in the number of the MC steps taken. The cause of this discrepancy is unknown except that the above analysis is based on non-interacting molecules, whereas the water molecules in our clusters are interacting and their virtual orbitals have significant amplitudes in the non-bonding region that need to be sampled.

The operational cost of each MC step is dominated by that of evaluating the integrands of Eqs. (8) and (9) at a point in the 13-dimensional parameter space. This in turn involves evaluating the numerical values of MO's at a point, each of which is defined as a linear combination of AO's. Hence, the overall cost should be asymptotically proportional to the number of MO's times, the number of AO's, and grows quadratically with size. In our program, however, we evaluate all AO's at the point and store them (at a linearly scaling cost) before they are used to generate the values of all MO's (at a quadratically scaling cost). In practice, the first step constitutes the hotspot and the overall cost exhibits a faster-than-quadratic scaling with size. The measured CPU times corroborate these expectations; the CPU time per MC step displays the size dependence that is in between linear and quadratic.

It must be cautioned, however, that comparing the linear-to-quadratic scaling of MC-MP2 and the quintic scaling of the conventional MP2 is unfair, given the presence and growth of the statistical uncertainty with size as well as the huge prefactor multiplying the scaling function of MC-MP2. Nonetheless, it should be clear from this study that the presented idea is feasible and holds an exceptional promise in the era of massively parallel supercomputers and should be fully developed for large molecules and solids.

IV. CONCLUSION

We have proposed and implemented a whole new algorithm of MP2 or a novel branch of QMC, in which the

Laplace-transformed expression of the MP2 energy is evaluated by MC integration at a computational cost per step that scales only quadratically with size. The usual hotspot of the MP2 algorithm, the integral transformation, and the need to store large amount of data (such as partially transformed integrals) are completely eliminated in our algorithm, allowing us to redesign the algorithms of an array of electron-correlation theories into simpler, potentially more efficient, and parallel-scalable ones although at present the conventional MP2 algorithms are still considerably faster for small molecules such as those studied here. The viability of the algorithm hinges on whether one can find a weight function that satisfies the requirements that it is analytically integrable, finite, and non-negative everywhere, and has the same singularities as the integrands. We have identified such functions and demonstrated their effectiveness.

ACKNOWLEDGMENTS

S.Y.W. and S.H. are supported by U.S. Department of Energy (DE-FG02-11ER16211). S.H. is a Camille Dreyfus Teacher-Scholar, a Scialog Fellow of Research Corporation for Science Advancement, and an Alumni Research Scholar of University of Illinois. S.Y.W. and K.S.K. are supported by Korean National Research Foundation (National Honor Scientist Program: 2010-0020414 and WCU: R32-2008-000-10180-0) and by Korea Institute of Science and Technology Information (KSC-2011-G3-02). We thank Dr. David M. Ceperley and Dr. Lucas K. Wagner for valuable technical advice.

- ¹R. J. Bartlett, *Annu. Rev. Phys. Chem.* **32**, 359 (1981).
- ²J. Almlöf, *Chem. Phys. Lett.* **181**, 319 (1991).
- ³M. H. Kalos and P. A. Whitlock, *Monte Carlo Methods* (Wiley-VCH, Weinheim, 2008).
- ⁴S. Obara and A. Saika, *J. Chem. Phys.* **84**, 3963 (1986).
- ⁵N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. N. Teller, and E. Teller, *J. Chem. Phys.* **21**, 1087 (1953).
- ⁶A. S. Kronrod, *Nodes and Weights of Quadrature Formulas. Sixteen-Place Tables* (Consultants Bureau, New York, 1965).
- ⁷H. Flyvbjerg and H. G. Petersen, *J. Chem. Phys.* **91**, 461 (1989).
- ⁸S. Suhai, *Phys. Rev. B* **27**, 3506 (1983).
- ⁹M. Head-Gordon, R. J. Rico, M. Oumi, and T. J. Lee, *Chem. Phys. Lett.* **219**, 21 (1994).
- ¹⁰S. Hirata, *J. Chem. Phys.* **122**, 094105 (2005).
- ¹¹S. Ten-no, *J. Chem. Phys.* **121**, 117 (2004).
- ¹²T. Shiozaki, E. F. Valeev, and S. Hirata, *Annu. Rep. Comp. Chem.* **5**, 131 (2009).
- ¹³A. J. W. Thom and A. Alavi, *Phys. Rev. Lett.* **99**, 143001 (2007).
- ¹⁴Y. Ohtsuka and S. Nagase, *Chem. Phys. Lett.* **463**, 431 (2008).
- ¹⁵G. H. Booth, A. J. W. Thom, and A. Alavi, *J. Chem. Phys.* **131**, 054106 (2009).
- ¹⁶D. Cleland, G. H. Booth, and A. Alavi, *J. Chem. Phys.* **132**, 041103 (2010).
- ¹⁷R. Blankenbecler, D. J. Scalapino, and R. L. Sugar, *Phys. Rev. D* **24**, 2278 (1981).
- ¹⁸G. Sugiyama and S. E. Koonin, *Ann. Phys. (N.Y.)* **168**, 1 (1986).
- ¹⁹S. Zhang and H. Krakauer, *Phys. Rev. Lett.* **90**, 136401 (2003).
- ²⁰D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980).
- ²¹B. L. Hammond, W. A. Lester, Jr., and P. J. Reynolds, *Monte Carlo Methods in Ab Initio Quantum Chemistry* (World Scientific, Singapore, 1994).
- ²²A. Luchow and J. B. Anderson, *Annu. Rev. Phys. Chem.* **51**, 501 (2000).
- ²³J. Kolorenc and L. Mitas, *Rep. Prog. Phys.* **74**, 026502 (2011).