

Projector Monte Carlo method based on Slater determinants: a new sampling method for singlet state calculations

Yuhki Ohtsuka · Shigeru Nagase

Received: 10 March 2011 / Accepted: 26 August 2011 / Published online: 16 September 2011
© Springer-Verlag 2011

Abstract A new sampling method is proposed for projector Monte Carlo (PMC) calculations based on Slater determinants (SD) in singlet states. Using the symmetry of the α and β electron determinants, the number of configurations to be considered can be about one-half of the original sampling. We applied the new sampling to the PMC-SD calculations of the H₂O molecule in the ground state. The results were always improved by the new sampling method both for the equilibrium and for bond-stretched structures.

Keywords Quantum Monte Carlo · New sampling method · Full-CI · Slater determinants · Singlet state calculation

1 Introduction

The diffusion Monte Carlo (DMC) method [1–5], also called the projector Monte Carlo (PMC) method, has attracted considerable interest recently because it is suitable for massively parallel calculations. The DMC method also has been known as a very accurate method that can simulate the exact solution of a Schrödinger equation. The numerically exact value is obtainable without limitations from basis set expansion because electrons are expressed as particles. Antisymmetry of electrons is considered using

the nodes of trial wave functions [6–8]. Consequently, the accuracy of the DMC method depends strongly on the accuracy of trial wave functions. Although this node-dependency can be reduced by optimization of trial wave functions using variational Monte Carlo techniques [9], it remains an important disadvantage of the DMC method.

To avoid the node-dependency on trial wave functions, we have proposed a PMC method based on configuration state functions (CSFs) [10] or Slater determinants (SDs) [11]. Using CSFs or SDs as walkers, the antisymmetry of electrons is satisfied automatically. Therefore, no additional information such as nodes of trial wave functions is required. The accuracy of the PMC method is improved systematically by increasing the number of walkers. It converges to the full configuration interaction (CI) as a limit. We have recently expanded the PMC-SD method to excited calculations [11]. Excited states are calculated state-by-state by eliminating the properties of the lower states from the imaginary-time propagator.

Recently, a very similar method, the full configuration interaction quantum Monte Carlo method [12], was reported by Alavi and coworkers for ground state calculations. In their method, the case where the transition of a walker is accepted and the case where the transition is rejected are considered separately. However, the definition of the transition probability and the sign of a newly generated walker are the same as ours. Their results show excellent agreement with the full-CI ones. They have also proposed an approximation to cut off of the walkers [13] and have shown the efficiency of such methods.

In this article, we propose a new sampling method for the PMC-SD calculations of singlet states to reduce computational costs. The number of configurations to be considered is considerably decreased using the symmetries of configurations, and the sampling efficiency is improved.

Dedicated to Professor Shigeru Nagase on the occasion of his 65th birthday and published as part of the Nagase Festschrift Issue.

Y. Ohtsuka (✉) · S. Nagase
Department of Theoretical and Computational Molecular
Science, Institute for Molecular Science,
Okazaki 444-8585, Japan
e-mail: ohtsuka@ims.ac.jp

Problems related to spin symmetry caused by statistical errors are also reduced.

2 Theory and algorithm

In the PMC-SD and PMC-CSF methods, the formal solution of the imaginary-time Schrödinger equation,

$$\Psi(\tau + \Delta\tau) = \exp(-\Delta\tau\hat{H})\Psi(\tau), \quad (1)$$

is simulated using the Monte Carlo method. For simplicity of integration, the imaginary-time propagator, $\exp(-\Delta\tau\hat{H})$, is truncated up to the linear terms as

$$\begin{aligned} \Psi(\tau + \Delta\tau) &= \exp(-\Delta\tau\hat{H})\Psi(\tau) \approx (1 - \Delta\tau\hat{H})\Psi(\tau) \\ &= \sum_{I,J} |I\rangle\langle I|(1 - \Delta\tau\hat{H})|J\rangle\langle J|\Psi(\tau) \\ &= \sum_{I,J} |I\rangle U^\dagger U \langle I|(1 - \Delta\tau\hat{H})|J\rangle U^\dagger U \langle J|\Psi(\tau) \\ &= \sum_{I'} |I'\rangle(1 - \Delta\tau E_{I'})\langle I'|\Psi(\tau), \end{aligned} \quad (2)$$

where $|I\rangle$ is a SD in the PMC-SD method, and where $E_{I'}$ and $|I'\rangle$, respectively, represent the I' - eigenvalue and eigenvector of Hamiltonian. $|I\rangle$ and $|I'\rangle$ are related by a unitary transformation (i.e., $U|I\rangle = |I'\rangle$). However, the converged eigenvector (wave function) is correct because the following relation is satisfied in Eq. 2 when time step $\Delta\tau$ is sufficiently small.

$$1 - \Delta\tau E_{0'} > 1 - \Delta\tau E_{1'} > 1 - \Delta\tau E_{2'} > \dots > 1 - \Delta\tau E_{N'} \quad (3)$$

Therein, $E_{0'}$ is the ground state energy.

In the PMC-SD method, the walkers of the Monte Carlo simulation are the electronic configurations expressed by SDs. The distribution of walkers is defined as

$$q = (n_0, n_1, n_2, \dots, n_N), \quad (4)$$

where n_I is the number of walkers whose configuration is $|I\rangle$. This distribution varies by the Monte Carlo simulation of the operation of the approximated imaginary-time propagator in Eq. 2. As presented in Fig. 1, the transition probability is defined as the matrix element of the imaginary-time propagator. We usually use configurations that are mutually orthonormal ($\langle I|J\rangle = \delta_{IJ}$). Therefore, the transition probabilities are proportional to the Hamiltonian matrix elements, as

$$\langle I|(1 - \Delta\tau\hat{H})|J\rangle = -\Delta\tau\langle I|\hat{H}|J\rangle. \quad (5)$$

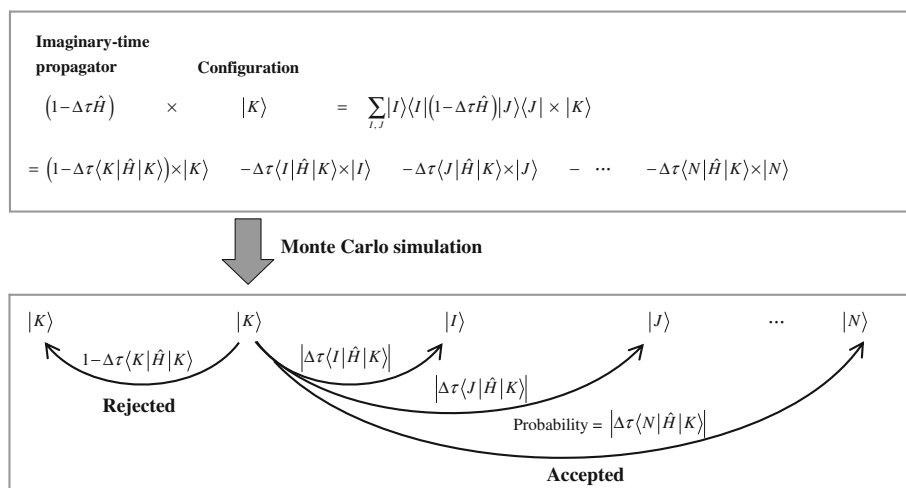
If a random number is smaller than the transition probability, then the transition is accepted. The detailed algorithm is presented in Fig. 1 of Ref. [10]. In one step, all walkers undergo this process.

The calculation proceeds as portrayed in Fig. 2. First, we prepare an initial distribution of walkers, which usually consists of only the HF configuration $|0\rangle$. In the next step, the configurations of some walkers change to others. After an adequate step, we can obtain a stationary distribution, which corresponds to the ground state wave function. The wave function is obtained using the normalization of summation of the distribution, as

$$\Psi_{\text{PMC-SD}} = \sum_I C_I |I\rangle = \frac{1}{\sqrt{\sum_I (n_I)^2}} \times \sum_I n_I |I\rangle. \quad (6)$$

Therefore, the coefficient of configuration $|I\rangle$ is proportional to the numbers of walkers whose configuration is $|I\rangle$ ($C_I \propto n_I$).

Fig. 1 Monte Carlo representation of operation of the imaginary-time propagator



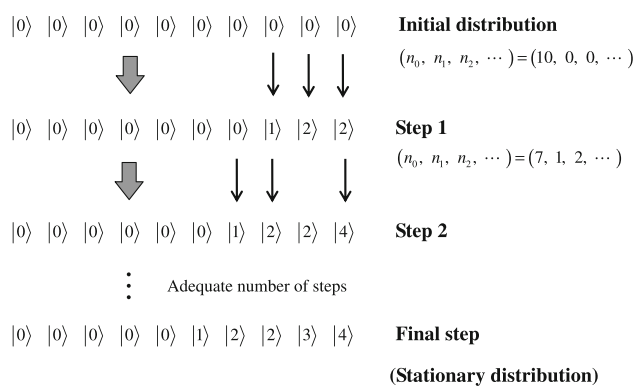


Fig. 2 Job stream of the PMC-SD calculation

The energy is calculated variationally in Ref. [10] as

$$E_{\text{PMC-SD}}(\text{variational}) = \langle \Psi_{\text{PMC-SD}} | \hat{H} | \Psi_{\text{PMC-SD}} \rangle. \quad (7)$$

We can also estimate the energy non-variationally using intermediate normalization as

$$E_{\text{PMC-SD}}(\text{non-variational}) = \langle 0 | \hat{H} | \Psi'_{\text{PMC-SD}} \rangle, \quad (8)$$

where $|0\rangle$ is usually the HF configuration. $|\Psi'_{\text{PMC-SD}}\rangle$ is the intermediate normalized wave function:

$$\begin{aligned} |\Psi'_{\text{PMC-SD}}\rangle &= |\Psi_{\text{PMC-SD}}\rangle / C_0 \\ &= 1.0|0\rangle + \frac{C_1}{C_0}|1\rangle + \frac{C_2}{C_0}|2\rangle + \dots + \frac{C_N}{C_0}|N\rangle. \end{aligned} \quad (9)$$

This energy is the same as the projected energy reported in Ref. [12]. The statistical errors of the non-variational energies are larger than those of the variational energies. However, the computational costs for the energy calculations are much smaller. In this article, all energies were calculated non-variationally.

In the PMC-SD method, the transition probabilities and energies are calculated more quickly than those of the PMC-CSF method because the Hamiltonian matrix elements between SDs are simpler than those between CSFs. However, the number of independent variables of SDs is larger than that of CSFs, and the spin symmetry is not usually conserved. Therefore, we introduce a new sampling to the PMC-SD method to reduce these problems using the symmetry of the α and β electron determinants in singlet states.

A Slater determinant or electronic configuration can be expressed as a combination of α and β electron determinants (α electron determinant) \times (β electron determinant). In the present program, the electronic configurations are stored as a two-dimensional array, $|I, J\rangle$, where I and J , respectively, denote the labels of α and β electron determinants: For example, the configuration $|1, 1\rangle$ represents the Hartree–Fock configuration. In an exact wave function

of singlet states, the coefficient of configuration $|I, J\rangle$ is the same as that of configuration $|J, I\rangle$. Therefore, we perform the Monte Carlo simulations using only configurations $|J, I\rangle$ whose labels satisfy $J \geq I$. The total number of configurations to be considered decreases from N^2 to $N \times (N + 1)/2$ if the space symmetry is not considered, where N is the number of the α electron determinants. When N is large, the total number of configurations becomes nearly one-half.

In the new sampling, all possible transitions from a configuration are considered as in the original (random) sampling. However, if the transition to configuration $|I, J\rangle$ ($I < J$) is allowed, it is stored as $|J, I\rangle$, which is justified by presuming that the walkers whose configuration is $|I, J\rangle$ ($I < J$) are hidden in the simulations and the number of hidden walkers whose configuration is $|I, J\rangle$ is set to be the same as that of $|J, I\rangle$. As depicted in Fig. 3, the transition from the hidden configuration $|I, J\rangle$ [solid arrow (I)] takes place at the same time when the transition from the configuration $|J, I\rangle$ [solid arrow (II)] occurs, which is verified because the transition probability from the configuration $|J, I\rangle$ to the hidden configuration $|K, L\rangle$, $-\Delta\tau \langle J, I | \hat{H} | K, L \rangle$, is equal to the transition probability from the hidden configuration $|I, J\rangle$ to configuration $|L, K\rangle$, $-\Delta\tau \langle I, J | \hat{H} | L, K \rangle$.

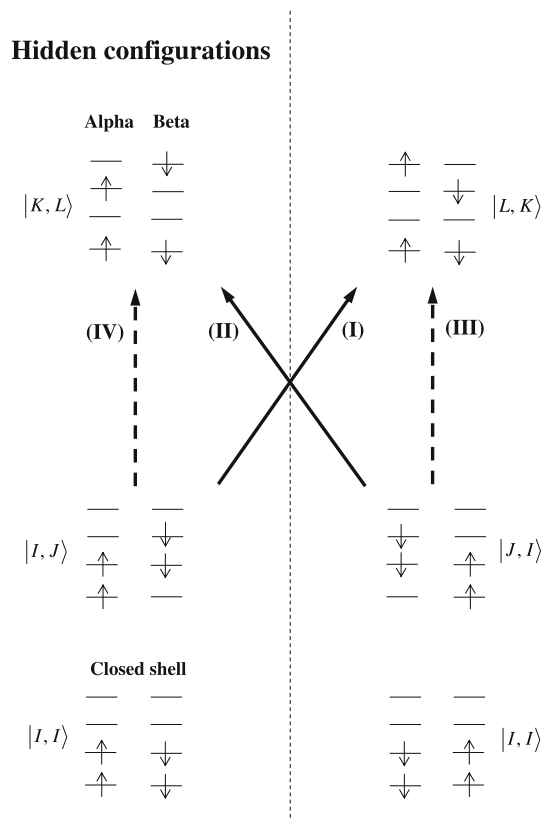


Fig. 3 Schematic representation of the transitions between configurations in the new sampling

Similarly, we presume that the transition between hidden configurations [dashed arrow (IV)] takes place when the transition from $|J, I\rangle$ to $|L, K\rangle$ [dashed arrow (III)] occurs to keep (the number of $|J, I\rangle =$ (the number of $|L, K\rangle$). For closed shell configurations, $|I, I\rangle$, one-half of the walkers are treated as hidden as depicted in Fig. 3.

When the wave function is constructed, the hidden configurations $|I, J\rangle$ are considered explicitly. The number of walkers whose configuration is $|I, J\rangle, n_{I,J}$, is set to be that of the configuration $|J, I\rangle, n_{J,I}$. The numbers of walkers whose configurations are closed shell, $|I, I\rangle$, are doubled because one-half of walkers are hidden in the simulation. As a result, the wave function is defined as follows.

$$\Psi_{\text{PMC-SD}} = \frac{2 \times \sum_I n_{I,I} |I, I\rangle + \sum_{J>I} n_{J,I} |J, I\rangle + \sum_{J>I} n_{J,I} |I, J\rangle}{\sqrt{\sum_I (2 \times n_{I,I})^2 + 2 \times \sum_{J>I} (n_{J,I})^2}} \quad (10)$$

It is noteworthy that the spin symmetry is conserved up to single excited configurations. In addition, triplet states are excluded from calculations because the coefficient of $|I, J\rangle$ is fixed to be the same as that of $|J, I\rangle$.

3 Results and discussion

The program of the developed PMC-SD method was implemented based on the GAMESS program package [14, 15]. In the present algorithm, molecular integrals are stored in memory. Then, the transition probabilities and weights are calculated from the molecular integrals each time as needed. The random numbers are generated using the Mersenne Twister method [16, 17].

We compared the PMC-SD results with the full-CI ones of H₂O in the ground state calculated by Olsen et al. [18]. The cc-pVDZ basis [19] was used; the numbers of molecular orbitals and the full-CI dimension (the number of independent configurations) were, respectively, 24 and about 4.5×10^8 . The time step ($\Delta\tau$) was fixed to 0.0002. For the Monte Carlo step number, 10,000 steps were used for the convergence to the stationary distribution, and the

PMC-SD energy was defined as the average energy over the subsequent 10,000 steps.

The PMC-SD energies and standard deviations are presented in Table 1. Three different numbers of walkers (2×10^7 , 4×10^7 , and 8×10^7) were used to examine the convergence against the number of walkers. They are, respectively, about 1/20, 1/10, and 1/5 of the full-CI dimension. For the original sampling, we did not obtain a stationary distribution for 2×10^7 walkers. For 4×10^7 and 8×10^7 walkers, the respective PMC-SD energies were -76.242 (2) and -76.2416 (5) Hartree. In both cases, the full-CI value (-76.241860 Hartree) [18] was reproduced within the statistical errors.

By the new sampling, a stationary distribution was obtained even for 2×10^7 walkers. The PMC-SD energies were, respectively, -76.240 (2), -76.2424 (8), and -76.2417 (3) Hartree for 2×10^7 , 4×10^7 , and 8×10^7 walkers. Although the average energies did not depend on the sampling methods to any great degree, the statistical errors became smaller by the new sampling. The standard deviations by the original sampling were, respectively, 2 and 0.5 mHartree for 4×10^7 and 8×10^7 walkers, whereas they were, respectively, 0.8 and 0.3 mHartree by the new sampling. By the new sampling, the number of the independent configurations becomes small. For that reason, the number of the walkers whose configurations are the same becomes larger. Therefore, the standard deviations are reduced by the new sampling. For example, the number of walkers whose configurations were the HF was about 108,000 for 4×10^7 walkers by the original sampling, but 570,000 by the new sampling.

We also calculated the expectation values of the S^2 operator, $\langle \Psi_{\text{PMC-SD}} | S^2 | \Psi_{\text{PMC-SD}} \rangle$, for the original and new samplings. The results for 4×10^7 walkers were 2.8×10^{-2} and 7.7×10^{-4} for the original and new samplings, respectively. The new sampling makes the expectation value much closer to zero for the pure spin state.

We applied this new sampling also to the bond-stretched structures of H₂O in the ground state to observe the effects on the multi-reference type wave functions. As discussed in Ref. [10], more walkers are usually required for bond-stretched structures to obtain accuracy similar to the

Table 1 Total energies (in Hartree) of the ground states of H₂O calculated using full-CI and PMC-SD methods using three different quantities of walkers

	Number of walkers in PMC-SD			Full-CI ^a
	2×10^7	4×10^7	8×10^7	
Original sampling	–	-76.242 (2)	-76.2416 (5)	-76.241860
New sampling	-76.240 (2)	-76.2424 (8)	-76.2417 (3)	–

^a Ref. [18]

Table 2 Total energies (in Hartree) of the ground states of H₂O as a function of O–H bond length (Number of walkers = 4×10^7)

	O–H bond length		
	$1 \times R_e$	$2 \times R_e$	$3 \times R_e$
Original sampling	–76.242 (2)	–75.953 (1)	–75.913 (2)
New sampling	–76.2424 (8)	–75.951 (1)	–75.912 (2)
Full-CI ^a	–76.241860	–75.951665	–75.911946

^a Ref. [18]

equilibrium structure in the PMC-SD method because it is more difficult to sample wave functions that are dominated by several configurations than to sample those dominated by one configuration. The results obtained using 4×10^7 walkers for the geometry whose O–H bond lengths are twice and three times as large as those of the equilibrium structure ($2 \times R_e$ and $3 \times R_e$) are presented in Table 2. To prepare good initial distributions, we performed the complete active space (CAS) CI calculations with six active orbitals and six active electrons. For $2 \times R_e$, the PMC-SD energies were –75.953(1) and –75.951(1) Hartree, respectively, by the original and new sampling methods. Although the standard deviations happened to be the same, the energy using the new sampling is closer to the full-CI value of –75.951665 Hartree. [18].

For the calculations at $3 \times R_e$, we took 20,000 steps for convergence and subsequent 30,000 steps for energy calculations. The energy convergence often becomes slow at bond-stretched structures because it remains difficult to obtain a good initial distribution by small CI calculations. In addition, small energy differences between the ground and excited states at the bond-stretched structure slow the convergence, as shown by Eq. 2. Even after convergence, the PMC-SD energy oscillated very slowly around the exact value, and therefore, we used a time step of 0.0005 that is larger than the case at $1 \times R_e$ and $2 \times R_e$. The PMC-SD energies were –75.913(2) and –75.912(2) Hartree, respectively, using the original and new sampling methods. The discrepancy by the original sampling from the full-CI value of –75.911946 Hartree [18] was about 1 mHartree. Although the standard deviations are similar, the new sampling method yielded a better result than that of original sampling.

4 Conclusion

We developed a new sampling method for the PMC-SD calculations of singlet states to reduce the computational costs. The number of configurations to be considered decreases according to the symmetry of α and β electron

determinants in a singlet state. The efficiency of sampling is thereby improved. We applied the new sampling to the PMC-SD calculations of H₂O in the ground state. The new sampling method always yielded better results both for the equilibrium and bond-stretched structures. For the spin symmetry, the lower triplet states can be excluded from calculations. Furthermore, the spin contamination can be reduced because the spin symmetry is conserved up to single excited configurations.

Acknowledgments This work was supported by a Grant-in-Aid for the Next Generation Super Computing Project (Nanoscience Program), specially Promoted Research, and Young Scientists (B) from MEXT of Japan. Some calculations were performed at the Research Center for Computational Science, Okazaki, Japan.

References

- Hammond BL, Lester WA Jr, Reynolds PJ (1994) Monte Carlo methods in ab initio quantum chemistry, World Scientific lecture and course notes in chemistry, vol 1. World Scientific, Singapore
- Anderson JB (2007) Quantum Monte Carlo origins, development, applications. Oxford University Press, Oxford
- Foulkes WMC, Mitas L, Needs RJ, Rajagopal G (2001) Rev Mod Phys 73:33
- Aspuru-Guzik A, Salomón-Ferrer R, Austin B, Perusquía-Flores R, Griffin MA, Oliva RA, Skinner D, Domin D, Lester WA Jr (2005) J Comput Chem 26:856
- Needs RJ, Towler MD, Drummond ND, López-Ríos P (2006) CASINO ver. 2.0.0 user manual. University of Cambridge, Cambridge
- Anderson JB (1976) J Chem Phys 65:4121
- Moskowitz JW, Schmidt KE, Lee MA, Kalos MH (1982) J Chem Phys 77:349
- Reynolds PJ, Ceperley DM, Alder BJ, Lester WA Jr (1982) J Chem Phys 77:5593
- Umrigar CJ, Toulouse J, Filippi C, Sorella S, Hennig RG (2007) Phys Rev Lett 98:110201
- Ohtsuka Y, Nagase S (2008) Chem Phys Lett 463:431
- Ohtsuka Y, Nagase S (2010) Chem Phys Lett 485:367
- Booth GH, Thom AJW, Alavi A (2009) J Chem Phys 131:054106
- Cleland D, Booth GH, Alavi A (2010) J Chem Phys 132:041103
- Schmidt MW, Baldrige KK, Boatz JA, Elbert ST, Gordon MS, Jensen JH, Koseki S, Matsunaga N, Nguyen KA, Su S, Windus TL, Dupuis M, Montgomery JA (1993) J Comput Chem 14:1347
- Gordon MS, Schmidt MW (2005) In: Dykstra CE, Frenking G, Kim KS, Scuseria GE (eds) Theory and applications of computational chemistry: the first forty years. Elsevier, Amsterdam, pp 1167–1189
- Matsumoto M, Nishimura T (1998) Mersenne Twister: A 623-dimensionally equidistributed uniform pseudorandom number generator. ACM Trans Model and Comp Simul 8(1):3–30
- Saito M, Matsumoto M (2008) SIMD-oriented fast mersenne twister: a 128-bit pseudorandom number generator, Monte Carlo and Quasi-Monte Carlo methods 2006. Springer, pp 607–622
- Olsen J, Jørgensen P, Koch H, Balkova A, Bartlett RJ (1996) J Chem Phys 104:8007
- Dunning TH Jr (1989) J Chem Phys 90:1007