

A Novel Exact Fixed-node Quantum Monte Carlo Algorithm

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Abstract: In this paper we proposed a novel exact fixed-node quantum Monte Carlo (EFNQMC) algorithm, which is a self-optimizing and self-improving procedure. In contrast to the previous EFNQMC method, the trial function is optimized synchronistically in the diffusion procedure, but not before the beginning of EFNQMC computation. In order to optimize the trial function, the improved steepest descent technique is used, in which the step size is automatically adjustable. The procedure is quasi-Newton and converges super linearly. We also use a novel trial function, which has correct electron-electron and electron-nucleus cusp conditions. The novel EFNQMC algorithm and the novel trial function are employed to calculate the energies of 1^1A_1 state of CH_2 , 1^1A_g state of C_8 and the ground-states of H_2 , LiH , Li_2 , H_2O , respectively. The test results show that both the novel algorithm and the trial function proposed in the present paper are very excellent.

Keywords: Self-optimizing, quantum Monte Carlo method, cusp conditions.

In our previous article¹, the exact fixed-node quantum Monte Carlo (EFNQMC) method has been proposed. It is proved that the value of the energy calculated using the traditional FNQMC method is only the zeroth order approximation of the eigenvalue of the energy, and the first order approximation value is¹:

$$E_1 = \overline{H}_1 - \frac{\left[\overline{H}_2 - (\overline{H}_1)^2 \right]^2}{\overline{H}_3 - 3\overline{H}_2\overline{H}_1 + 2(\overline{H}_1)^3} \quad (1)$$

There are several obstacles in the EFNQMC calculation: (I) Before the beginning of EFNQMC computation, the parameters of the trial function ψ_T must have been optimized by the variational Monte Carlo (VMC) method. Optimization of these parameters is both time-consuming and expensive. (II) The optimization is not efficient, because there are two different samplings required in the VMC and EFNQMC methods. (III) Previously, Umrigar *et al.*, Bueckert *et al.*² have proposed methods for optimizing the trial functions. Umrigar *et al.* employed the variance minimization technique over a fixed set of configurations of the electron samples from $|\psi_T|^2$. In practice there is a "weight ill-condition" about the node of the trial function². A steepest descent

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technique was employed by Bueckert *et al.*. The technique converges linearly, and even for the optimization of a quadratic function it often converges very slowly and encounters the ill-condition, especially near the optimum point.

In this paper we propose a novel approach for improvement of the EFNQMC method, which has the following advantages: (I) It is a self-optimizing diffusion procedure. In the novel EFNQMC computation, the parameters of the trial function ψ_T are optimized synchronistically in the diffusion procedure. It is economical in CPU time. (II) This novel algorithm is a self-improving Monte Carlo scheme. With this method one could construct well-behaved trial function and improve the accuracy and convergence of EFNQMC computations. (III) In order to optimize the trial function, the improved steepest descent technique is used, in which the step size is automatically adjustable. The procedure is quasi-Newton and converges super linearly.

The self-optimizing EFNQMC approach can be summarized as follows:

(i) Select N diffusion particles as a set of initial configurations according to the trial function $\Psi_T(P_{K=0}, R)$. We call the initial configurations a configuration block 0. At the end of the 0 block parameter P is updated, as follows:

$$P_{k=1} = P_{k=0} - \lambda_0 \left(\frac{\overline{(E_L - E_T) \frac{\partial E_L}{\partial P}}}{\left(\overline{\left(\frac{\partial E_L}{\partial P} \right)^2} \right)} \right)_{k=0} \quad (2)$$

and thus one obtains a new $\Psi_T(P_{K=1}, R)$. In preceding text, λ_0 is a step-size factor, E_L is the “local energy” and E_T is the “trial energy”.

(ii) Pick the mth configuration from the configuration block. The electrons diffuse independently for a small time τ , according to the Gaussian part of the Green’s function¹. After the N configurations in the block were diffused, a new configuration block (block 1) is formed.

(iii) Use next equation over block 0 and 1 to calculate $P_{k=2}$ and a newer $\Psi_T(P_{K=2}, R)$ can be obtained.

$$P_{k+1} = P_k - \frac{1}{2} \left\{ \frac{\overline{(E_L - E_T) \frac{\partial E_L}{\partial P}}}{\left(\overline{\left(\frac{\partial E_L}{\partial P} \right)^2} \right)} \right\}_k \times \frac{(P_k - P_{k-1})^T \cdot \left\{ \left[(E_L - E_T) \frac{\partial E_L}{\partial P} \right]_k - \left[(E_L - E_T) \frac{\partial E_L}{\partial P} \right]_{k-1} \right\}}{\left\{ \left[(E_L - E_T) \frac{\partial E_L}{\partial P} \right]_k - \left[(E_L - E_T) \frac{\partial E_L}{\partial P} \right]_{k-1} \right\}^T \cdot \left\{ \left[(E_L - E_T) \frac{\partial E_L}{\partial P} \right]_k - \left[(E_L - E_T) \frac{\partial E_L}{\partial P} \right]_{k-1} \right\}} \quad (3)$$

(iv) Repeat steps (ii) and (iii) until the steady state is reached.

During the self-optimizing diffusion process the following aspects should be noted: (I) The “trial energy” E_T is estimated by the average of E_L from a prior block. So E_T and the block are updated synchronistically. (II) In the course of a circle if $\lambda \leq 0$, let $\lambda = 0.05 \sim 0.1$, and then restart the circle. (III). The criterion of convergence is chosen as $\Delta E_T = 10^{-5}$.

In the former articles^{3,4}, we use Jastrow function as the correlation function. It is well known that the correlation function only contains the correct electron-electron cusp condition and not the electron-nucleus cusp condition. The later is more important, because the probability of the electron and nucleus approaching each other is much larger than that of two electrons approaching. In the present paper we use a novel correlation function proposed by Boys and Handy⁵, which has correct electron-electron and electron-nucleus cusp conditions. Results of sample calculations, as shown later, indicate that this type of correlation function, if employed in EFNQMC runs, is capable of giving much more accurate results.

In order to test the correctness of the novel EFNQMC method, the values of the zeroth and the first approximation of the energies of 1^1A_1 state of CH_2 , 1A_g (C_{4h} , acet) state of C_8 and the ground-states of H_2 , LiH , Li_2 , H_2O have been calculated using the self-optimizing procedure. The geometrical configurations of these states were given in the literature¹. HF-B type function is used as a trial function Ψ for the novel EFNQMC method. The values of the zeroth and the first approximation of the energies for these states calculated using the novel EFNQMC method, E_0 and E_1 , are given in **Table 1**. For the convenience of comparison, **Table 1** also lists the values of the energies for these states calculated using H-F, CI and the ordinary EFNQMC methods¹. In addition, the experimental data, which are taken from the literatures¹, of the values of these energies are given in **Table 1**, where the percentage listed below each datum is a percentage of the electronic correlation energy, which is corresponding to the datum. It can be seen from the data given in **Table 1** that for 1^1A_1 state of CH_2 , 1A_g (C_{4h} , acet) state of C_8 and the ground-states of H_2 , LiH , Li_2 , H_2O the calculation only needs to be in progress until the first approximation when using our novel EFNQMC method. All the percentages of the electronic correlation energy are over 96%, which much better than the values calculated using CI and the ordinary EFNQMC methods (ε_1 is the first approximation data calculated using the ordinary EFNQMC method). For example, for C_8 molecule the energy values obtained using the CI method, the ordinary EFNQMC methods (ε_1) and the novel EFNQMC algorithm (E_1) are -303.436, -304.258 and -304.3342 (a. u.), respectively. The percentages of the correlation energy recovered by these different methods are 52.34%, 92.77% and 98.58%, respectively. The exact nonrelativistic energy is -304.361(a. u.), and Hartree-Fock energy is -302.47567 (a. u.). It can also be seen, for C_8 , that the novel EFNQMC algorithm in the present paper recovers the correlation energies of 1.7331 and 1.8577 (a. u.) for E_0 and E_1 , the percentages of the correlation energy recovered by E_0 and E_1 are 91.97% and 98.58%, and there are very small statistical errors of 0.0004 (a. u.) and 0.0006 (a. u.), respectively. While the previous EFNQMC method¹ gave the correlation energies of 1.691, 1.748 and 1.847 (a. u.) for ε_0 , ε_1 and ε_2 with the errors of 0.004, 0.006 and 0.008 (a. u.), the percentages of the correlation energy recovered by ε_0 , ε_1 and ε_2 are 89.75%, 92.77 and 97.99%, respectively. For the data of other molecules shown in **Table 1**, a similar analysis can be performed. In a word, the novel EFNQMC algorithm, compared with the previous EFNQMC method, has a higher accuracy and a smaller statistical error. These results show that the algorithm described in this paper is very successful.

Table 1 Energies (a.u.) of 1^1A_1 state of CH_2 , $1A_g$ (C_{4h} , acet) state of C_8 and the ground states of H_2 , LiH , Li_2 , H_2O calculated from the ordinary and novel EFNQMC methods.

	$1^1A_1(CH_2)$	$1A_g(C_8)$	H_2	LiH	Li_2	H_2O
Exp.	-39.133	-304.361	-1.17447	-8.07021	-14.9954	-76.4376
H-F	-38.8944	-302.477	-1.1336	-7.987	-14.872	-76.0675
CI	-39.0272	-303.436	-1.1737	-8.0647	-14.903	-76.3683
	55.66%	52.34%	98.12%	93.38%	25.12%	81.28%
the ordinary method						
0	-39.092(3)	-304.168(4)	-1.1744(3)	-8.0468(2)	-14.9818(4)	-76.231(2)
	82.79%	89.75%	99.83%	71.86%	88.98%	44.17%
1	-39.112(3)	-304.258(6)		-8.0691(3)	-14.9901(6)	-76.375(3)
	91.07%	92.77%		98.67%	95.71%	83.09%
the novel method						
E_0	-39.1072(5)	-304.2097(4)	-1.1745(2)	-8.0610(2)	-14.9844(1)	-76.3308(2)
	89.07%	91.97%	99.91%	88.99%	91.08%	71.15%
E_1	-39.1261(4)	-304.3342(6)		-8.0685(2)	-14.9933(2)	-76.4264(5)
	97.11%	98.58%		97.95%	98.31%	96.98%

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