Articles

A Novel Method for Fixed-node Quantum Monte Carlo

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In this paper, a novel method for fixed-node quantum Monte Carlo is given. By comparing this method with the traditional fixed-node one, this novel method can be applied to calculate molecular energy more exactly. An expansion of the eigenvalue of the energy for a system has been derived. It is proved that the value of the energy calculated using the traditional fixed-node method is only the zeroth order approximation of the eigenvalue of the energy. But when using this novel method, in the case of only increasing less computing amounts (<1%), the first order approximation, the second order approximation, and so on can be obtained conveniently withr the detailed equations and steps in the practical calculation to calculate the values of the zeroth, first and second 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, and H_2O The results indicate that for these states it needs only the second order approximation to obtain over 97% of electronic correlation energy, which demonstrates that this novel method is very excellent in both the computing accuracy and the amount of calculation required.

Keywords Fixed-node, quantum Monte Carlo method, electronic correlation energy

Introduction

The fixed-node quantum Monte Carlo (FNQMC) method is one of the simplest and most widely used methods in various Monte Carlo procedures of solving Schrödinger equation. Some previous literatures[1,2] reported the comments about FNQMC method. In the practical calculation for FNQMC method, in general, a minimal basis set of Slater-type atomic orbital (STAO) and Jastrow functions are taken to constitute a trial function in order to decrease the computing amount. But in such case the accuracy of the calculation is affected. For example, the ground-state energy of H_2O molecule calculated using such trial function in the traditional FNQMC procedure gave only 43.9% of the electronic correlation energy. But the electronic correlation energy percentage obtained using the best CI method[3] was 81.2%.

In this paper, a novel FNQMC method is given. The electronic correlation energy percentage obtained using the novel FNQMC method can be increased until 95—100%, with but very little increase in computational cost (<1%). Thus, this novel FNQMC method is called the exact FNQMC (EFNQMC) method. Two ideas have been employed in the accomplishment of our goal. (1) Derivation of an expansion of the eigenvalue of the energy for a system. It is demonstrated that the value of the energy calculated using the traditional FNQMC method is only the first term in this expansion, namely, the value of the energy calculated using the traditional FNQMC method is only the zeroth order approximation of the real value of the energy for a system. (2) Presentation of the detailed equations and steps used for calculating the second term, the third term, and so on, in this expansion. It is interesting that this calculation can be carried out only using the configurations obtained after a diffusion process of the traditional FNQMC method has been completed. Hence, by comparing this novel FNQMC method with the traditional FNQMC method, in the case of almost no increase in the amount of calculation, the first order approximation, the second order approximation, and so on, of the real value of the energy can be calculated conveniently. Therefore, in principle, the

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accuracy for the calculation by EFNQMC method can be close to 100%.

In order to test the correctness of the novel FNQMC method, the values of the zeroth, the first and the second 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, and H_2O have been calculated using the novel FNQMC method. The results indicate that for these states, when using EFNQMC method, it needs only the second order approximation to obtain over 97% of electronic correlation energy with the amounts of calculation required being almost the same as those required when using the traditional FNQMC method, which demonstrates that this novel method is very excellent in both the computing accuracy and the amount of calculation required.

Calculation

Expansion equation of the eigenvalue of energy

$\boldsymbol{H}$ represents Hamilton operator for a system, and its eigenfunctions and eigenenergies are ϕ_i, $E_i(i=0,1,2,\cdots)$. If φ_A is a trial function for the FNQMC method, and φ_B is an "exact wave function" which has the same node structure as that possessed by φ_A, and possesses "node approximation",[3] then

$$\overline{H}_i = \frac{\langle \varphi_A | \boldsymbol{H}_i | \varphi_B \rangle}{\langle \varphi_A | \varphi_B \rangle} \qquad (i=0,1,2,\cdots) \tag{1}$$

Let us define an integral $F(t)$ containing parameter t,

$$F(t) = \frac{\left\langle \varphi_A \middle| \sum_{n=0}^{\infty} \frac{(-t)^n}{n!} \boldsymbol{H}^{n+1} \middle| \varphi_B \right\rangle}{\left\langle \varphi_A \middle| \sum_{n=0}^{\infty} \frac{(-t)^n}{n!} \boldsymbol{H}^{n} \middle| \varphi_B \right\rangle} = \frac{\sum_{n=0}^{\infty} \frac{(-t)^n}{n!} \overline{H}_{n+1}}{\sum_{n=0}^{\infty} \frac{(-t)^n}{n!} \overline{H}_n} \tag{2}$$

It can be proved that if φ_A and φ_B are non-zero overlapped with ϕ_0, then

$$\lim_{t\to\infty} F(t) = E_0 \tag{3}$$

Eq. (3) can be proved as follows. If both φ_A and φ_B are expanded with the eigenfunctions, ϕ_i, then

$$\varphi_A = \sum_i a_i \phi_i \tag{4}$$

$$\varphi_B = \sum_i b_i \phi_i \tag{5}$$

By substituting Eq. (4) and (5) into Eq. (2), the following equation can be obtained:

$$\begin{aligned} F(t) &= \frac{\left\langle \sum_i a_i\phi_i \middle| \sum_{n=0}^{\infty} \frac{(-t)^n}{n!} \boldsymbol{H}^{n+1} \middle| \sum_j b_j\phi_j \right\rangle}{\left\langle \sum_i a_i\phi_i \middle| \sum_{n=0}^{\infty} \frac{(-t)^n}{n!} \boldsymbol{H}^{n} \middle| \sum_j b_j\phi_j \right\rangle} \\ &= \frac{\left\langle \sum_i a_i\phi_i \middle| \sum_j b_j \left[\sum_{n=0}^{\infty} \frac{(-t)^n}{n!} (E_j)^{n+1} \right] \phi_j \right\rangle}{\left\langle \sum_i a_i\phi_i \middle| \sum_j b_j \left[\sum_{n=0}^{\infty} \frac{(-t)^n}{n!} (E_j)^{n} \right] \phi_j \right\rangle} \\ &= \frac{\sum_i a_i^* b_i E_i \exp(-E_i t)}{\sum_i a_i^* b_i \exp(-E_i t)} \\ &= \frac{\sum_i a_i^* b_i E_i \exp[-(E_i - E_0)t]}{\sum_i a_i^* b_i \exp[-(E_i - E_0)t)]} \end{aligned} \tag{6}$$

When the orthonormality of the set of the eigenfunction is applied to derivation of Eq. (6), then

$$\lim_{t\to\infty} F(t) = \frac{a_0^* b_0 E_0}{a_0^* b_0} = E_0 \tag{7}$$

If φ_A and φ_B are orthogonal to ϕ_0, respectively, and are non-zero overlapped with ϕ_1, using the same way, then

$$\lim_{t\to\infty} F(t) = E_1 \tag{8}$$

The second expression for $F(t)$ is introduced below. According to the principle on the FNQMC method,[3] the whole space can be divided (except for the position of the nodes) into a number of smaller space elements, Δv, and these smaller space elements can be placed in each area encircled by the boundary of the node of φ_A. In each space element, there is

$$\boldsymbol{H}(\varphi_B)_\nu = \varepsilon_\nu(\varphi_B)_\nu \tag{9}$$

where ε_ν is an approximate value of the energy in a space element, $\Delta\nu$. Consequently, $F(t)$ for the fixed-node method can be represented as follows:

$$\begin{aligned} F(t) &= \frac{\left\langle \phi_A \left| \sum_{n=0}^{\infty} \frac{(-t)^n}{n!} \boldsymbol{H}^{n+1} \right| \phi_B \right\rangle}{\left\langle \phi_A \left| \sum_{n=0}^{\infty} \frac{(-t)^n}{n!} \boldsymbol{H}^{n} \right| \phi_B \right\rangle} \\ &= \frac{\sum_\nu (\phi_A)_\nu^* \left[\sum_{n=0}^{\infty} \frac{(-t)^n}{n!} \boldsymbol{H}^{n+1} (\phi_B)_\nu \right] \Delta\nu}{\sum_\nu (\phi_A)_\nu^* \left[\sum_{n=0}^{\infty} \frac{(-t)^n}{n!} \boldsymbol{H}^{n} (\phi_B)_\nu \right] \Delta\nu} \\ &= \frac{\sum_\nu (\phi_A)_\nu^* \left[\sum_{n=0}^{\infty} \frac{(-t)^n}{n!} \varepsilon_\nu^{n+1} (\phi_B)_\nu \right] \Delta\nu}{\sum_\nu (\phi_A)_\nu^* \left[\sum_{n=0}^{\infty} \frac{(-t)^n}{n!} \varepsilon_\nu^{n} (\phi_B)_\nu \right] \Delta\nu} \\ &= \frac{\sum_\nu \varepsilon_\nu (\varphi_A^* \varphi_B)_\nu \exp(-\varepsilon_\nu t) \Delta\nu}{\sum_\nu (\varphi_A^* \varphi_B)_\nu \exp(-\varepsilon_\nu t) \Delta\nu} \end{aligned} \tag{10}$$

By analyzing the forms of the numerator and denominator in Eq. (10), it is evident that $F(t)$ can be expanded into the following form:

$$F(t) = \sum_{j=0}^{\infty} \alpha_j \exp(-\beta_j t) \tag{11}$$

Because $\lim F(t) \to E_0$ when $t \to \infty$, Eq. (11) can be further written as

$$F(t) = E_0 + \sum_{j=0}^{\infty} \alpha_j \exp(-\beta_j t) \tag{12}$$

In Eq. (12), both α_j and β_j are coefficients, and $\beta_j \geq 0$, thus, by treating Eq. (12) further the following equation can be obtained:

$$\begin{aligned} F(t) &= E_0 + \sum_{j=1}^{\infty} \sum_{i=0}^{\infty} \left[\frac{\alpha_j \beta_j^i}{i!} (-t)^i \right] \\ &= \left(E_0 + \sum_{j=1}^{\infty} \alpha_j \beta_j^0 \right) + \sum_{i=1}^{\infty} \left[\left(\sum_{j=1}^{\infty} \alpha_j \beta_j^i \right) \frac{(-t)^i}{i!} \right] \end{aligned} \tag{13}$$

Eq. (13) is the second expansion for $F(t)$. Of course, it can only be applied to the FNQMC method.

The third expansion for $F(t)$ is given below. Assuming

$$F(t) = \sum_{j=0}^{\infty} \frac{(-t)^i}{i!} P_i \tag{14}$$

and comparing Eq. (14) with Eq. (2), Eq. (15) can be obtained:

$$\frac{\sum_{n=0}^{\infty} \frac{(-t)^n}{i!} \overline{\boldsymbol{H}}_{n+1}}{\sum_{j=0}^{\infty} \frac{(-t)^j}{j!} \overline{\boldsymbol{H}}_j} = \sum_{j=0}^{\infty} \frac{(-t)^i}{i!} P_i \tag{15}$$

From Eq. (15), Eq. (16) can be derived:

$$\begin{aligned} \sum_{n=0}^{\infty} \frac{(-t)^n}{n!} \overline{\boldsymbol{H}}_{n+1} &= \left[\sum_{i=0}^{\infty} \frac{(-t)^i}{i!} P_i \right] \left[\sum_{j=0}^{\infty} \frac{(-t)^j}{j!} \overline{\boldsymbol{H}}_j \right] \\ &= \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \frac{(-t)^{i+j}}{i!j!} \overline{\boldsymbol{H}}_j P_i \end{aligned} \tag{16}$$

By assuming $n = i + j$, then, $j = n - i$. Thus, Eq. (16) can be written as the following form:

$$\sum_{n=0}^{\infty} \frac{(-t)^n}{n!} \overline{\boldsymbol{H}}_{n+1} = \sum_{n=0}^{\infty} (-t)^n \left[\sum_{i=0}^{n} \frac{\overline{\boldsymbol{H}}_{n-i}}{i!(n-i)!} P_i \right] \tag{17}$$

By comparing the left side of the equal sign with its right side for Eq. (17), Eq. (18) can be obtained:

$$\begin{aligned} \frac{\overline{\boldsymbol{H}}_{n+1}}{n!} &= \sum_{i=0}^{n} \frac{\overline{\boldsymbol{H}}_{n-i} P_i}{i!(n-i)!} \\ &= \frac{\overline{\boldsymbol{H}}_0}{n!} P_n + \sum_{i=0}^{n-1} \frac{\overline{\boldsymbol{H}}_{n-i} P_i}{i!(n-i)!} \end{aligned} \tag{18}$$

Because $\overline{\boldsymbol{H}}_0 = 1$, then

$$P_n = \overline{\boldsymbol{H}}_{n+1} - n! \sum_{i=0}^{n-1} \frac{\overline{\boldsymbol{H}}_{n-i}}{i!(n-i)!} P_i \tag{19}$$

Eq. (19) is a recursion equation of P_n in the third expansion, Eq. (14), for $F(t)$. Because $P_n = \overline{\boldsymbol{H}}_1$, from Eq. (19) P_n can be derived with various ranks below

$$\left.\begin{aligned} P_1 &= \overline{H}_2 - (\overline{H}_1)^2 \\ P_2 &= \overline{H}_3 - 3\overline{H}_2\overline{H}_1 + 2(\overline{H}_1)^3 \\ P_3 &= \overline{H}_4 - 4\overline{H}_3\overline{H}_1 - 3(\overline{H}_2)^2 + \\ &\quad 12\overline{H}_2(\overline{H}_1)^2 - 6(\overline{H}_1)^4 \\ P_4 &= \overline{H}_5 - 5\overline{H}_4\overline{H}_1 - 10\overline{H}_3\overline{H}_2 + \\ &\quad 20\overline{H}_3(\overline{H}_1)^2 + 30(\overline{H}_2)^2\overline{H}_1 - \\ &\quad 60\overline{H}_2(\overline{H}_1)^3 + 24(\overline{H}_1)^5 \\ &\cdots \end{aligned}\right\} \quad (20)$$

Since the P_n with various ranks in Eq. (20) has been established, the third expansion, Eq. (14), for $F(t)$ has also be established. From Eq. (3) and (14), Eq. (21) can be derived:

$$\lim_{t\to\infty} F(t) = \lim_{t\to\infty}\Big[P_0 + \sum_{i=1}^{\infty}\frac{(-t)^i}{i!}P_i\Big] = P_0 + \lim_{t\to\infty}\Big[\sum_{i=1}^{\infty}\frac{(-t)^i}{i!}P_i\Big] = E_0 \quad (21)$$

namely

$$E_0 - P_0 = \lim_{t\to\infty}\Big[\sum_{i=1}^{\infty}\frac{(-t)^i}{i!}P_i\Big] \quad (22)$$

It can be seen From Eq. (22) that $(E_0 - P_0)$ has some function dependency with $(P_1, P_2, \cdots)$. Assuming such function dependency is

$$P_0 - E_0 = \sum_{k=1}^{\infty} f_k(P_1 P_2, \cdots) \quad (23)$$

where f_k is some uncertain function form, the function form below can be established according to the relation between the second expansion and third expansion for $F(t)$. Let the second expansion [Eq. (13)] be combined with the third expansion [Eq. (14)], then

$$P_0 + \sum_{i=1}^{\infty}\Big[\frac{(-t)^i}{i!}P_i\Big] = (E_0 + \sum_{j=1}^{\infty}\alpha_j\beta_j^0) + \sum_{i=1}^{\infty}\Big[\frac{(-t)^i}{i!}(\sum_{j=1}^{\infty}\alpha_j\beta_j^i)\Big] \quad (24)$$

By comparing the left side of the equal sign with its right side for the above equation, Eq. (24), the resultant equation can be as follows:

$$P_0 - E_0 = \sum_{j=1}^{\infty}\alpha_j\beta_j^0 \quad (25)$$

$$P_i = \sum_{j=1}^{\infty}\alpha_j\beta_j^i \qquad (i = 1,2,\cdots) \quad (26)$$

For convenience of discussing the following problems, let

$$Q_0 = P_0 - E_0 \quad (27)$$

$$Q_i = P_i \qquad (i = 1,2,\cdots) \quad (28)$$

By using Eq. (27) and (28), Eq. (23) can be written as

$$Q_0 = \sum_{k=1}^{\infty} f_k(Q_1, Q_2, \cdots) \quad (29)$$

By combining Eq. (25) and Eq. (26), the following Eq. (30) can be obtained:

$$Q_0 = \sum_{j=1}^{\infty}\alpha_j\beta_j^i \qquad (i = 0,1,2,\cdots) \quad (30)$$

From Eq. (30) the following parameter, S_i, can be defined and studied:

$$\begin{aligned} S_i &= Q_iQ_{i+2} - Q_{i+1}^2 \\ &= (\sum_{j=1}^{\infty}\alpha_j\beta_j^i)(\sum_{k=1}^{\infty}\alpha_k\beta_k^{i+2}) - (\sum_{j=1}^{\infty}\alpha_j\beta_j^{i+1})(\sum_{k=1}^{\infty}\alpha_k\beta_k^{i+1}) \\ &= \sum_{j=1}^{\infty}(\sum_{k=1}^{\infty}[\alpha_j\alpha_k(\beta_k^2 - \beta_j\beta_k)](\beta_j\beta_k)^i \\ &= (\sum_{l=1}^{\infty}A_l\beta_l^i \qquad (i = 0,1,2,\cdots) \end{aligned} \quad (31)$$

In Eq. (31), α_j and β_j are some certain coefficients, and the definitions of A_l and B_l are as follows:

$$\left.\begin{aligned} A_{\frac{(j+k-2)(j+k-1)}{2}+j} &= \alpha_j\alpha_k(\beta_k^2 - \beta_j\beta_k) \\ B_{\frac{(j+k-2)(j+k-1)}{2}+j} &= \beta_j\beta_k \end{aligned}\right\} \quad (32)$$

It should be noted that both Eq. (31) and (30) have completely identical form. Thus, it can be thought that the function dependency between S_0 and $(S_1, S_2, \cdots)$ is completely equivalent to the function dependency between Q_0 and $(Q_1, Q_2, \cdots)$, namely

$$S_0 = \sum_{k=1}^{\infty} f_k(S_1, S_2, \cdots) \tag{33}$$

where those f_k in Eq. (33) are also the f_k in Eq. (29), which are some uncertain function forms, which will be established below.

According to $S_i = Q_iQ_{i+2} - Q_{i+1}^2$, Eq. (33) can be rewritten as

$$Q_0Q_2 - Q_1^2 = \sum_{k=1}^{\infty} f_k(Q_1Q_3 - Q_2^2, Q_2Q_4 - Q_3^2, \cdots) \tag{34}$$

Namely

$$Q_0 = \frac{Q_1^2}{Q_2} + \frac{1}{Q_2}\sum_{k=1}^{\infty} f_k(Q_1Q_3 - Q_2^2, Q_2Q_4 - Q_3^2, \cdots) \tag{35}$$

By comparing Eq. (35) with Eq. (29), those uncertain function forms f_k can be obtained:

$$f_1(Q_1, Q_2, \cdots) = \frac{Q_1^2}{Q_2} \tag{36}$$

$$f_{k+1}(Q_1, Q_2, \cdots) = \frac{1}{Q_2} f_k(Q_1Q_3 - Q_2^2, Q_2Q_4 - Q_3^2, \cdots) \quad (k = 1,2,\cdots) \tag{37}$$

Eq. (37) is a recursion equation for the uncertain function f_k with various ranks. From Eq. (36) and (37) Eq. (38) can be obtained:

$$f_2(Q_1, Q_2, \cdots) = \frac{1}{Q_2}\frac{(Q_1Q_3 - Q_2^2)^2}{Q_2Q_4 - Q_3^2} \tag{38}$$

$$f_3(Q_1, Q_2, \cdots) = \frac{1}{Q_2}\cdot\frac{1}{Q_2Q_4 - Q_3^2}\cdot \frac{[(Q_1Q_3 - Q_2^2)(Q_3Q_5 - Q_4^2) - (Q_2Q_4 - Q_3^2)^2]^2}{(Q_2Q_4 - Q_3^2)(Q_4Q_6 - Q_5^2) - (Q_3Q_5 - Q_4^2)^2} \tag{39}$$

From Eq. (27)—(29), and (36)—(39) the expansion of the eigenvalue of the energy can be obtained for a system:

$$E_0 = P_0 - \frac{P_1^2}{P_2} - \frac{1}{P_2}\frac{(P_1P_3 - P_2^2)^2}{P_2P_4 - P_3^2} - \frac{1}{P_2}\frac{1}{P_2P_4 - P_3^2}\cdot \frac{[(P_1P_3 - P_2^2)(P_3P_5 - P_4^2) - (P_2P_4 - P_3^2)^2]^2}{(P_2P_4 - P_3^2)(P_4P_6 - P_5^2) - (P_3P_5 - P_4^2)^2} - \cdots \tag{40}$$

Eq. (40) is an equation of calculating the exact energy, E_0, for a system using the fixed-node method. As can be seen from Eq. (20), if the values of $\overline{H_i}$ can be obtained with various ranks, the values of P_i with various ranks can also be calculated. Then, the exact value, E_0, of the energy can be obtained from Eq. (40).

It must be pointed out that because $P_0 = \overline{H_1}$ and $\overline{H_1}$ is the value of the energy calculated using the traditional FNQMC method, this value is only the zeroth approximation of the exact value of the energy for a system. It can be seen from Eq. (40) that if the second term, the third term, and so on, have been calculated, the first approximation, the second approximation, and so on, of the exact value of the energy can be obtained for a system.

EFNGMC *method*

If φ_A represents a trial function for the fixed-node method, and φ_B is an "exact wave function" which possesses the same node structure as that possessed by φ_A and has "node approximation", the samples can be taken from the system with $\frac{\varphi_A\varphi_B}{\int \varphi_A\varphi_B d\tau}$ after the diffusion process has been completed according to the fixed-node method principle. Therefore, the $\overline{H_i}$ defined previously by us can be calculated as follows:

$$\overline{H_i} = \frac{\int \varphi_A H_i \varphi_B d\tau}{\int \varphi_A\varphi_B d\tau} = \sum_c \left(\frac{H_i\varphi_A\varphi}{A}\right)_c = \sum_c (E_L^{(i)})_c \tag{41}$$

where c represents the configuration obtained after the diffusion process has reached equilibrium, and $E_L^{(i)}$ is the local energy for rank i defined in our previous paper.[4,5] The following calculation equation was given in our previous paper.

$$E_L^{(i+1)} = E_L^{(1)}E_L^{(i)} - 0.5\nabla_N^2 E_L^{(i)} - \nabla_N \ln\varphi_A \cdot \nabla_N E_L^{(i)} \quad (42)$$

As can be seen from Eq. (40) and (41), calculating the first approximation, the second approximation, and so on, of the eigenenergy for a system using EFNQMC method need not revise the traditional FNQMC program, but only need calculate them according to the original FNQMC process. When the diffusion steps end and after calculating the value of $E_L^{(i)}$ (this calculation is essential for the traditional FNQMC method), the values of E_L can be calculated for various ranks by the method. It is evident that an increase in the computing amount can be completely neglected.

Results and discussion

In order to test the correctness of the novel FNQMC method, the values of the zeroth, first and second 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, and H_2O have been calculated using EFNQMC method. The geometrical configurations of these states were given in the literature.[4-6] HF·J type function is used as trial function φ_A for EFNQMC method, *i.e.*

$$\varphi_A = D^{\uparrow} D^{\downarrow} \exp\left(\sum_{i<j} \frac{a_{ij}r_{ij}}{1 + br_{ij}}\right) \quad (43)$$

where $D^{\uparrow(\downarrow)}$ denotes the up (down) spin-state determinant which is constructed from the molecular orbital based on a minimal basis set of STO, r_{ij} represents the distance between electrons i and j, $a_{ij} = 1/4$ (when i and j have the same spin) or $a_{ij} = 1/2$ (when i and j have the contrast spin), and $b = 1$.[4]

The numbers of the initial configuration taken are 1000 (H_2), 5000 (CH_2, LiH and Li_2) and 10000 (C_8 and H_2O), and the time step is 0.005/h (H_2), 0.001/h (CH_2, LiH and Li_2) and 0.0001/h (C_8 and H_2O). The time of calculation required on a P111 computer is 11 min (H_2), 92 min (LiH), 135 min (Li_2), 185 min (CH_2), 448 min (H_2O) and 2356 min (C_8, a PIV computer), respectively. The values of the zeroth, first and second approximation of the energies for these states calculated using EFNQMC method, ε_0, ε_1 and ε_2, 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 FNQMC methods.[3,5,6] In addiion, the experimental data, which are taken from the literatures,[3,5,6] of the values

Table 1 Energies (hartrees) 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, and H_2O calculated from several methods

	1 $^1A_1$ (CH_2)	^1A_g (C_{4h}, acet)	H_2	LiH	Li_2	H_2O
Experimental	-39.133[a]	-304.361[b]	-1.17447[c]	-8.07021(5)[c]	-14.9954[c]	-76.4376[c]
H-F limit	-38.8944[a]	-302.477[b]	-1.1336[c]	-7.987[c]	-14.872[c]	-76.0675[c]
Best CI	-39.0272[a]	-303.436[b]	-1.1737[c]	-8.0647[c]	-14.903[c]	-76.3683[c]
	55.66%	52.34%	98.12%	93.38%	25.12%	81.28%
FNQMC (minimal basis set of STO)			-1.1745(8)[c]	-8.047(5)[c]	-14.985(5)[c]	-76.23(2)[c]
			100%	72.11%	91.57%	43.91%
EFNQMC (this work)						
ε_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%
ε_1	-39.112(3)	-304.25(6)	-8.0691(3)	-14.9901(6)	-76.375(3)	
	91.07%	92.77%	98.67%	95.71%	83.09%	
ε_2	39.128(5)			-304.323(8)	-14.9933(8)	-76.430(3)
	97.77%	97.99%			98.29%	97.88%

[a] Data from Ref. 5; [b] Data from Ref. 6; [c] Data from Ref. 3.

of these energies are given in Table 1, where the percentage listed below each datum is a percentage of the electronic correlation energy, 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, and H_2O the calculation only needs to be in progress until the second approximation when using our novel FNQMC method. All the percentages of the electronic correlation energy are over 97%, much better than the values calculated using

CI and the traditional FNQMC methods (ε_0 is the datum calculated using the traditional FNQMC method). For example, for LiH, Li_2 and H_2O molecules the best percentages of the electronic correlation energy calculated using CI method are 93.38%, 25.12% and 81.28%, respectively, and the data of the electronic correlation energy calculated using the traditional FNQMC method are only 72.11%, 91.57% and 43.91%, respectively. It is noted that the time spent on the computer when using EFNQMC method is almost the same as that spent when using the traditional FNQMC method. This clearly shows the advantage given with EFNQMC method. It can also be seen from Table 1 that the percentages of the electronic correlation energy of $1\ ^1A_1$ state of CH_2 and $^1A_g(C_{4h}$, acet) state of C_8 calculated using the traditional FNQMC method are 82.79% and 89.75%, respectively. It is evident that EFNQMC method is also very excellent for the excited state and macromolecules. It is more important that the trial function for EFNQMC method does not need to be optimized in Monte Carlo process, and the optimization of the trial function in Monte Carlo process is very inconvenient and spends too much time on a computer.[7]

It must be pointed out that the CMX method[8] put forward by Cioslowski is similar to EFNQMC method. CMX method is also to expand the eigenvalue of energy, E, into the same progression form of $\overline{H_i}$ $(i = 1,2,\cdots)$, and then to obtain the approximate value of the energy by calculating the values of $\overline{H_i}$ $(i = 1,2,\cdots)$. But EFNQMC method is different from CMX method with the differences being: (1) that the definition of $\overline{H_i}$ $(i = 1,2,\cdots)$, is different, for CMX method: $\overline{H_i} = <\Psi_t|H_i|\Psi_t>/<\Psi_t|\Psi_t>$, where Ψ_t represents a trial function. But the definition of $\overline{H_i}$ for EFNQMC method is $\overline{H_i} = <\Psi_t|H_i|\Psi_0>/<\Psi_t|\Psi_0>$, where Ψ_0 is an "exact wave function" which possesses the same node structure as that possessed by the trial function Ψ_t, and possesses node approximation; (2) that $\overline{H_i}$ for EFNQMC method is calculated after the diffusion has been completed, and this is very easy to do. But it is very difficult to calculate $\overline{H_i}$ for CMX method; (3) that the speed of convergence of the progression for EFNQMC method is much faster than this for CMX method. This is because the zeroth approximation $\overline{H_1}$ of the eigenvalue of the energy, E, for EFNQMC method is very close to the eigenvalue of the energy, and CMX method does not possess such character; (4) that the values of $\overline{H_i}$ $(i = 1,2,\cdots)$ for EFNQMC method are limited and can be calculated. If Ψ_A is a trial function for the FNQMC method, and Ψ_B is an "exact wave function" which has the same node structure as that possessed by Ψ_A, and possesses the node approximation, according to the FNQMC method principle the whole space can be divided (except for the position of the node) into a number of smaller space elements, $\Delta\nu$, and these space elements can be put in each area encircled by the boundary of the node of Ψ_A, respectively. For each space element, $\Delta\nu$:

$$\boldsymbol{H}(\Psi_B)_\nu = \varepsilon_\nu(\Psi_B)_\nu \tag{44}$$

where ε_ν represents an approximate value of the energy in a space element, $\Delta\nu$. Thus, the value of $\overline{H_i}$ is as follows

$$\overline{H_i} = \frac{<\Psi_A|H_i|\Psi_B>}{<\Psi_A|\Psi_B>} = \frac{\sum_\nu (\Psi_A)_\nu^* H_i(\Psi_B)_\nu \Delta\nu}{\sum_\nu (\Psi_A)_\nu^* (\Psi_B)_\nu \Delta\nu} = \frac{\sum_\nu (\Psi_A)_\nu^* (\Psi_B)_\nu \varepsilon_\nu^i \Delta\nu}{\sum_\nu (\Psi_A)_\nu^* (\Psi_B)_\nu \Delta\nu} \tag{45}$$

Because each term of calculating the summation in Eq. (45) is limited, the value of $\overline{H_i}$ is also limited and can be calculated.

As described above, EFNQMC method is a convenient and timesaving one with excellent calculation accuracy. This novel method will be able to be expanded to calculate exactly the energies for the excited state and macromolecules.

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