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Fixed-node Quantum Monte Carlo: A Novel Approach

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Abstract: In this paper, a novel method for fixed-node quantum Monte Carlo is given. We have derived an expansion of the eigenvalue of the energy for a system and proved that the value of the energy calculated using the traditional fixed-node quantum Monte Carlo method is only the zero order approximation of the eigenvalue of the energy. But when using our novel method, in the case of only increasing less computing amounts (<1%), we can obtain conveniently the first order approximation, second order approximation, and so on. We have calculated the values of the zero, first and second approximation ($_{0,}$ $_1$ and $_2$) of the energies of 1^1A_1 state of CH_2, ^1A_g (C_{4h}, acet) state of C_8 and the ground-state of H_2O using this novel method. The results indicate that for 1^1A_1 state of CH_2, ^1A_g (C_{4h}, acet) state of C_8 and the ground-state of H_2O it needs only the second order approximation to obtain electronic correlation energy with over 97%. This 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.

The fixed-node quantum Monte Carlo (FNQMC)[1,2] method has made it possible to calculate the electronic structure of relatively large molecular systems. These large systems range from positron complexes [NH_2, Ps] with ~10 electrons to C_{20} isomers with 120 electrons, silicon crystal structures of 250 atoms and 1000 valence electrons. In the practical calculation for FNQMC method, in general, a minimal basis set of Slater-type atomic orbital (STO) 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 with such trial function in the traditional FNQMC procedure gives the electronic correlation energy only with 43.9%. But the electronic correlation energy obtained by the best CI method[2] is 81.2%. The novel FNQMC procedure put forward by us can give the electronic correlation energy as high as 95-100%. We have derived 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, it is only the zero order approximation of the real value of the energy for a system. We have also derived the detailed equations and steps for calculating the second and third term in this expansion. Hence, by this novel FNQMC method the first order one, the second order approximation of the real value of the energy can be calculated conveniently almost without increasing in the amount of calculation. Therefore, in principle, the accuracy for the calculation of this novel FNQMC method is close to 100%.

H represents Hamilton operator for a system, and its eigenfunctions and eigenenergies are ($_i$, E$_i$, I = 0, 1, 2..). If $_A$ is a trial function for the FNQMC method, and $_B$ is an "exact" wave function which has the "node approximation"[2], we have

$$\overline{H_i} = \frac{\langle j_A | H^i | j_B \rangle}{\langle j_A | j_B \rangle} \qquad (I = 0, 1, 2..) \tag{1}$$

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

$$F(t) = \frac{\left\langle j_A \left| \sum_{n=0}^{\infty} \frac{(-t)^n}{n!} H^{n+1} \right| j_B \right\rangle}{\left\langle j_A \left| \sum_{n=0}^{\infty} \frac{(-t)^n}{n!} H^{n} \right| j_B \right\rangle} = \frac{\sum_{n=0}^{\infty} \frac{(-t)^n}{n!} \overline{H_{n+1}}}{\sum_{n=0}^{\infty} \frac{(-t)^n}{n!} \overline{H_n}} \tag{2}$$

We can prove that if $_A$ and $_B$ are non-zero overlap with $_0$, then

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

If $_A$ and $_B$ are orthogonal to $_0$, respectively, and are non-zero overlap with $_1$, we can demonstrate

$$\lim_{t\to\infty} F(t) = E_1 \qquad \ldots\ldots \tag{4}$$

According to the CMX method principle[3], we have:

$$\lim_{t\to\infty} F(t) = P_0 - \frac{P_1^2}{P_2} - \frac{1}{P_2}\frac{(P_1P_3 - P_2^2)^2}{P_2P_4 - P_3^2} - \frac{1}{P_2}\frac{1}{P_2P_4 - P_3^2}\frac{\left[(P_1P_3 - P_2^2)(P_3P_5 - P_4^2) - (P_2P_4 - P_3^2)^2\right]^2}{(P_2P_4 - P_3^2)(P_4P_6 - P_5^2) - (P_3P_5 - P_4^2)^2} - \cdots \tag{5}$$

In Eq. 5 $P_0 = E_L^{(1)}$

$$P_n = E_L^{(n+1)} - n!\sum_{i=0}^{n-1} \frac{E_L^{(n-i)}}{i!(n-i)!} P_i \qquad (n = 1, 2,..) \tag{6}$$

One can judge from Eqs. (3) to (6) that calculation of the value of the nth order approximation of the eigenenergy only requires calculation of $E_L^{(i)}$ (I = 1, 2,..2n+1). According to the fixed-node method principle, we can calculate the values of E_L for various ranks when the diffusion steps have finished. The increase of the computing amount can be completely neglected. In order to test the correctness of the novel FNQMC method, the values of the zero, first and second approximation ($_0$, $_1$ and $_2$) of the energies of 1 $^1A_1$ state of CH_2, ^1A_g (C_{4h}, acet) state of C_8 and the ground-state of H_2O have been calculated using this method. $_2$ are given in **Table 1**. For the convenience of comparison, **Table 1** also lists the values calculated using H-F and CI method. In **Table 1** the percentage listed is a percentage of the electronic correlation energy. The geometrical configurations of these molecules were given in the literature[1,4,5]. HF J type function[6] is used as a trial function $\boldsymbol{j}_A$ for the novel FNQMC method. 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-state of H_2O the calculation only needs to be proceed until the second approximation and all the percentages of the electronic correlation energy are over 97%. This is much better than the values calculated using CI and the traditional FNQMC methods ($_0$ is the data calculated using the traditional FNQMC method). This clearly shows the advantage of our novel FNQMC method. It is more important that the trial function for the novel FNQMC method does not need to be optimized in Monte Carlo process.

Conclusion

The novel FNQMC method can be used in calculation of first and second order approximation of the real value of the energy without increasing in amount of calculation with excellent calculation accuracy.

Table 1 The energies (hartrees) of 1 $^1A_1$ state of CH_2, ^1A_g (C_{4h}, acet) state of C_8 and the ground state of H_2O calculated from several methods

	1 $^1A_1$ (CH_2)	^1A_g (C_{4h}, acet)	H_2O
Experimental	-39.133	-304.361	-76.4376
H-F limit	-38.8944	-302.477	-76.0675
Best CI	-39.0272	-303.436	-76.3683
CI (%)	55.66 %	52.34 %	81.28%
$_0$ (this work)	-39.092(3)	-304.168 (4)	-76.231 (2)
$_0$ (%)	82.79%	89.75%	44.17%
$_2$ (this work)	-39.128 (5)	-304.323 (8)	-76.430 (6)
$_2$ (%)	97.77%	97.99%	97.88%

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