

OPTIMIZATION OF TRIED WAVE FUNCTION IN QUANTUM MONTE CARLO METHOD*

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ABSTRACT

A method for optimizing tried wave functions in quantum Monte Carlo method has been found and used to calculate the energies of molecules, such as H_2 , Li_2 , H_3^+ , H_3 and H_4 . Good results were obtained.

Keywords: Monte Carlo method, optimization.

I. PRINCIPLE

The quantum Monte Carlo (QMC) method is a new calculation method in quantum mechanics developed during recent years. How to select tried wave function is one of the important problems in this method. The optimization method of tried wave function will be investigated in this paper.

A good tried wave function should have proper nodes, which leads to rapid convergence and a small square deviation of energy. Generally, the tried wave function is obtained from the traditional *ab initio* calculation represented by Slater's determinants of single-electron wave functions. This tried wave function can also be multiplied by a correlation function^[1-3] (electron-electron and nucleus-nucleus),

$$S = \prod_{i,j} S_{ij},$$

$$S_{ij} = 1 - a \exp\left(-\frac{r_{ij}}{b_1} - \frac{r_{ij}}{b_2}\right), \quad (1)$$

where $b_1 = 2a_1/(1 - a_1)$ (the cusp condition), r_{ij} is the distance between two electrons (or an electron and a nucleus). Being multiplied by a fixed factor, the original optimization single-electron wave function will be disturbed to some extent. The previous molecular orbital linear combination coefficients, the atomic orbital exponents and parameters a_1 , b_1 and b_2 in the correlation function need to be further optimized.

What is the most important for the optimization of statistics problems is to

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eliminate thoroughly the influence of statistics errors. The average energy of a system, on the one hand, depends on the parameter C of the tried wave function and on the other hand, it relates to the coordinate R (all the multi-electron coordinates), i.e. $E = E(C, R)$. Especially, when a small number of samples are taken, the dependence of E on R is still more evident. For some samples, the energy value can be improved by increasing a certain parameter, but for others, the result is reverse. If this error is decreased by increasing the number of samples, the procedure will become very tedious. Then, how can we lessen the error caused by a decreasing number of samples? We propose a method for comparing the values of different parameters at a single sample based on the same Markov process. The factor influencing the statistical energy is limited to the adjustable parameter C with which the influence of R is counteracted reciprocally. This method will be introduced in detail.

Let vector

$$C = (C_1, C_2, \dots, C_m) \quad (2)$$

be the parameters to be optimized. A disturbed parameter is defined as

$$C_i = (C_1, C_2, \dots, C_i + \Delta C_i, \dots, C_m). \quad (3)$$

Substituting C_i into the tried wave function, we obtain

$$\Psi_i \equiv \Psi_i(c_i, R), \quad i = 1, 2, 3, \dots, m. \quad (4)$$

The local energy is calculated from $E_L^{(i)} = \hat{H}\Psi_i/\Psi_i$, and the deviation resulting from R is eliminated. However, the distribution function of the Markov process is not derived from Ψ_i , but from Ψ_g which takes the undisturbed tried wave functions $\Psi_i = \Psi_i(c, R)$. In order to obtain reasonable results, E_i must be multiplied with a weight $\omega_i \equiv (\Psi_i/\Psi_g)^2$, then

$$\langle E_i \rangle = \frac{\sum_i \omega_i E_L^{(i)}}{\sum_i \omega_i} = \frac{\langle \Psi_i | \hat{H} | \Psi_0 \rangle}{\langle \Psi_i | \Psi_0 \rangle}. \quad (5)$$

Within a certain snapshot (about 200—500 steps, after statistically averaging E_i , the derivatives of energy with respect to various parameters are calculated with the difference method and the most rapid direction declining is found out to be

$$N = \left(-\frac{\partial E}{\partial c_1}, -\frac{\partial E}{\partial c_2}, \dots, \frac{\partial E}{\partial c_m} \right). \quad (6)$$

Various parameters are adjusted along this direction once again, i.e.

$$C' = C + \alpha N,$$

where α is the step factor which may change with different parameters and generally take 2—10% of the reference value.

The advantage of this method is that the adjustment of each parameter can be carried out before the entire statistics process is accomplished. In the snapshot of a Markov process, an incomplete statistics may be carried out. Although this statistics process does not make any energy converge, some valuable information on the adjustment

of parameters can be obtained from the sensitivity of energy difference to various parameters. Furthermore, even if the adjustment at a step is wrong, during the accumulation of such processes, the right optimization direction will be finally reached.

The processes of optimization are shown as follows:

(1) A $3n$ -dimensional electron coordinate configuration is derived from a random number, and is changed by random walks and quantum force resulting from the induced tried wave functions. Its growth or death is determined by branches. This is called one of the steps of the Markov process. Whether this step is acceptable or not may be determined by the rules in Ref. [1]

(2) Taking 200—500 steps as a snapshot, we make statistics of energy by Eq. (5) for this snapshot (called the snapshot energy).

(3) From the difference of snapshot energies, we get derivatives with respect to every parameter and find out the direction of the fastest declining rate, and then slightly adjust all the parameters along this direction.

(4) Continuing this Markov process and taking the following snapshot, we make statistics and adjust parameters till the energy converges.

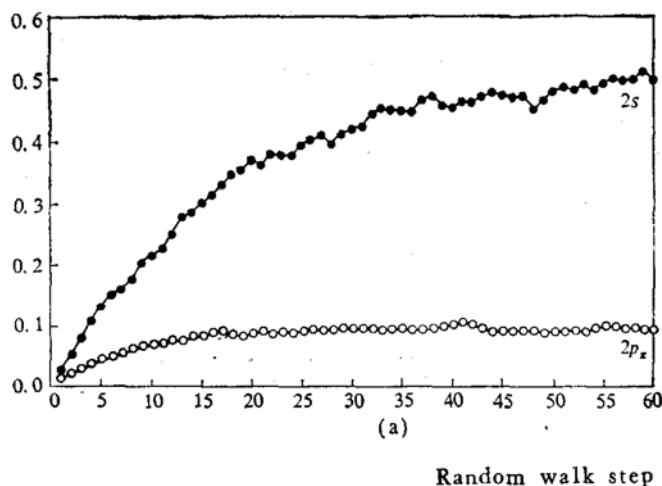


Fig. 1(a). Optimal process of $2s$ and $2p_x$ linear coefficients (ground-state H_2).

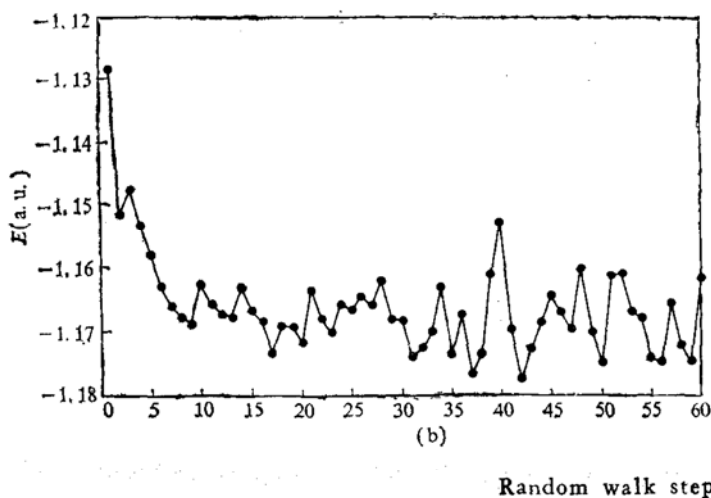


Fig. 1(b). Optimal process of energy for ground-state H_2 .

II. APPLICATIONS

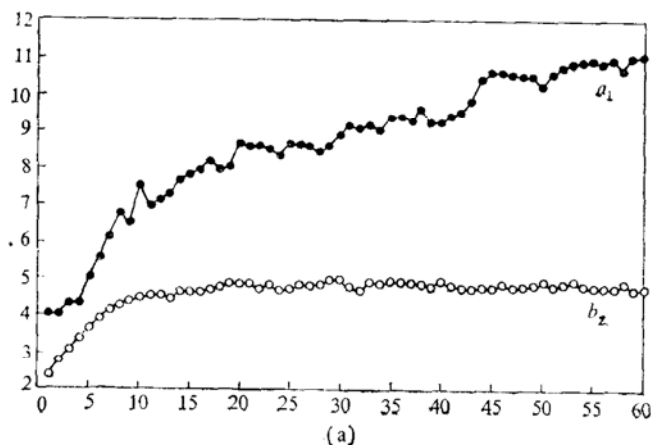
(1) $H_2(x)$ and Li_2 molecules in the ground state

In the ground state of H_2 molecule, both electrons are located in σ_g molecular orbitals which are combined linearly by the atomic orbitals $1s$, $2s$ and $2p_z$ (their orbital exponents are $\zeta_{1s} = 1.0$, $\zeta_{2s} = 1.64$, and $\zeta_{2p} = 2.0$). Because of the symmetry the combination coefficients of the two $1s$ (and $2s$) orbitals are the same, and so are those of two $2p_z$ orbitals. The value of the two $2p_z$ orbitals are the same while their signs are reverse. When the coefficients of $1s$ orbitals are chosen, the six combination coefficients are reduced to four, i.e. two $2s$ and two $2p_z$ orbitals.

Fig. 1(a) shows the optimization process of the two coefficients in 60 snapshots. The final equilibrium values are 0.47 and 0.08, respectively.

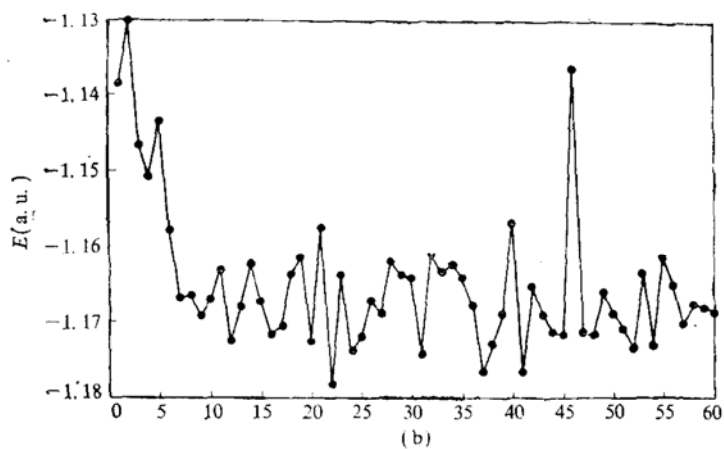
Fig. 2(a) shows the optimization process of the parameters a_1 and b_1 of the electron correlation function.

The above two figures show clearly that despite the great fluctuations caused



Random walk step

Fig. 2(a). Optimal process of parameters a_1 and b_2 (ground-state H_2).



Random walk step

Fig. 2(b). Optimal process of energy for ground-state H_2 .

by samples in the energy values in these figures, the stable improvement of parameters is not affected, and the value of energy tends to be stable. This means that the influence of samples is counter-balanced as designed in our method.

The second-order parameter b_2 of the electron correlation function in Fig. 2(a) is not sensitive to the improvement of energy. In the first ten snapshots, the value of statistics energy declined evidently with the improvement of a_1 , and then maintained a certain value. Although the a_1 value rose up continuously in the following snapshots and reached 11.03, the b_2 value remained 0.47. This result is the same as that of the Li_2 molecule (see Fig. 3(a)).

The energy given by the tried wave function which is formed by the above optimized parameters is -1.1680 a.u., while that of QMC is -1.1745 a.u., very close to the actual value, -1.17453 a.u.

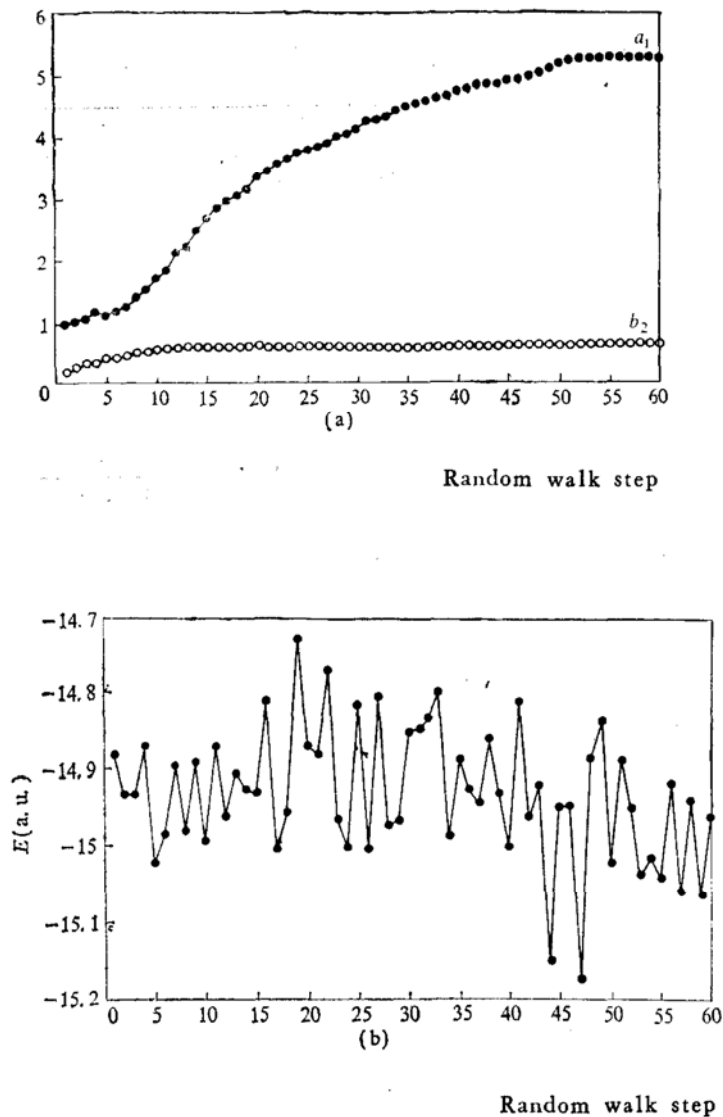


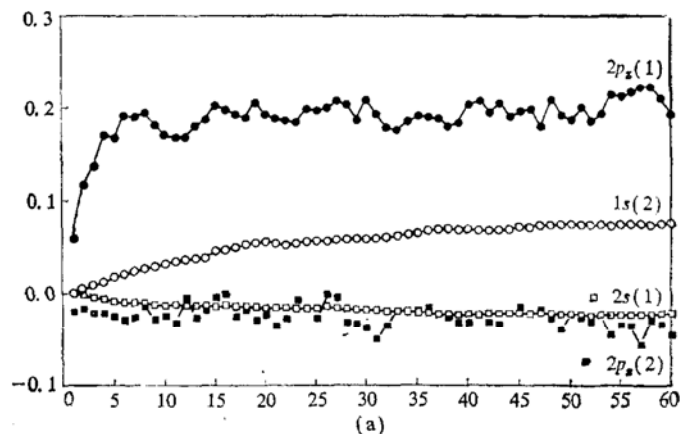
Fig. 3.(a) Optimal process of parameters a_1 and b_2 (ground-state Li_2).
(b) Optimal process of energy for ground-state Li_2 .

Fig. 3 shows the optimization process of 2-electron correlation parameters of Li_2 molecule. The final results are $b_2 = 9.5$ and $a_1 = 0.42$. The variation energy is -14.9390 a.u., while that of QMC is -14.98 a.u. The actual value is -14.9967 a.u.

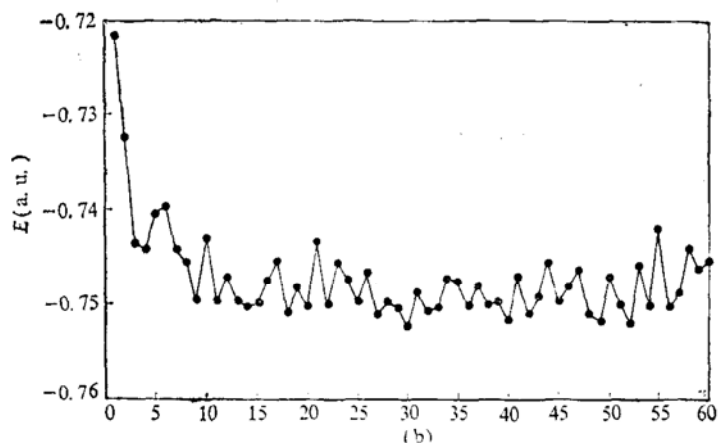
(2) $\text{H}_2(\text{B})$ molecule in the excited state

The QMC method can calculate the energies in ground states. Under the circumstances of orthogonality of molecular orbitals, it can also calculate the energies in excited states. Taking $\text{H}_2(\text{B})$ as an example, besides σ_g orbitals, σ_u orbitals may be formed by two independent coefficients, so there are four independent parameters to be optimized. Fig. 4(a) show their optimization process. From this figure, it is found that the two s -orbital coefficients change stably, while the two p -orbital coefficients change with great undulation, showing that the proportion of $2p$ orbital is more important in the calculation.

Although the $2p$ -orbital coefficients are small, they influence the energy value evidently. The variation energy is -0.7479 a.u., while that of QMC is -0.7565 a.u. which is almost 100% of the correlation energy.



Random walk step



Random walk step

Fig 4(a). Optimal process of four linear coefficients (excited-state H_2).
(b) Optimal process of energy for excited-state H_2 .

(3) H_3^+ , H_3 and pyramid-type H_4 molecules

Table 1 lists the energy values of the two lowest energy levels E' and A'_1 of H_3^+ and H corresponding to different equilateral-triangle side lengths.

Table 1
Total Energies of H_3^+ and H_3 Molecules (a.u.) (D_{3h})

R (a.u.)	$H_3(E')$	$H_3(A'_1)$	$H_3(A'_1)$
1.65	-1.5354(V) -1.5586(Q)		-1.3327(V) -1.3433(Q)
1.655	-1.5363(V) -1.5626(Q)	-1.4493(V) -1.4822(Q)	-1.3317(V) -1.3433(Q)
1.70	-1.5400(V) -1.5694(Q)	-1.4426(V) -1.4745(Q)	-1.3317(V) -1.4319(Q)

Note: (V) and (Q) represent the variation Monte Carlo energy value and quantum Monte Carlo energy value, respectively.

During recent years, more and more attention has been paid to type H molecule. Experiments^[4] have proved that the efficiency of annihilating excited $H_2(B)$ molecules by ground $H_2(X)$ molecules is ten times that of annihilation by He. In addition, Nicolaides^[5] stated that there exists an evident electronic transfer that forms local-ionization when the four H atoms form a regular pyramid based on an equilateral triangle. When the side length of the triangle is 1.70 a.u., close to the equilibrium distance of H_3^+ and the vertical distance D between the H atoms on the top of pyramid, and the ground face is 3.8 a.u., the avoided crossing appears on the potential curve (dotted line in Fig. 5), and the excited-state curve exhibits shallow maximum corresponding to a second stable state in excited state. This assumption, if true, would open a new channel for seeking fuel.

We calculated the potential-energy curve for the above configuration. The obtained energy value was lower than the above mentioned, thus indicating that under

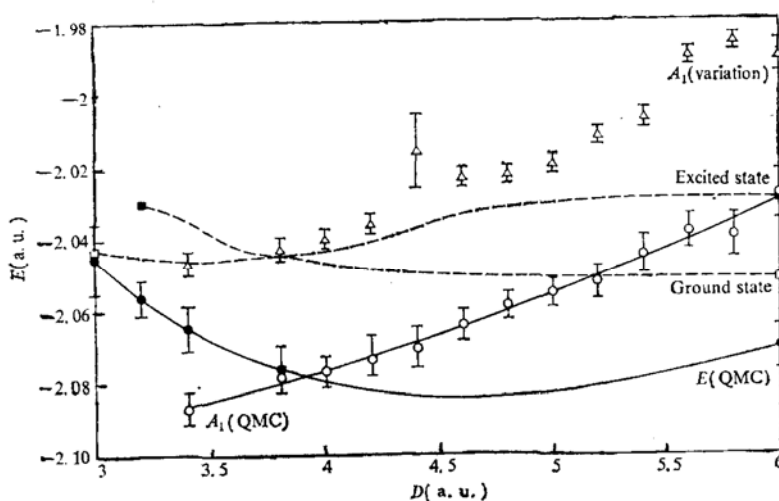


Fig. 5. Potential energy curve for molecule H_4 .

the condition of C_{3v} symmetry, the avoided crossing of a curve does not exist, there is only a curve-crossing of E -state curve with another curve in A_1 state. Only when the symmetry of geometric configuration lowers, may one of the energy curves of E avoid crossing the energy curve of A_1 , but the other curve keeps on crossing that of A_1 .

III. CONCLUSIONS

QMC has been proved to be capable of accurately calculating small molecules systems. By means of optimized trial wave functions, we can obtain 40—80% correlation energy in variation Monte Carlo and 80—100% correlation energy in QMC. The optimization technique we developed can calculate not only the energy in ground state but also the energy of excited state. The acquired optimized wave function may be used to calculate some quantities, such as dipole moment and transition moment.

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