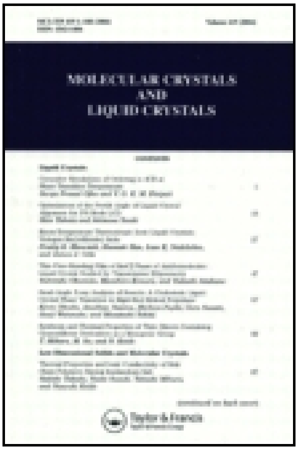

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CALCULATION OF MAGNETIZATION BY PATH INTEGRAL METHOD II

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Abstract

Theoretical treatment based on the path integral method were presented and applied to calculations for the magnetization. Numerical calculation is performed by the Monte Carlo method. In this paper this method is applied to the simple system i.e. methyl and hydrogen radical pair as a extended model from the hydrogen molecule system in the series paper entitled "part I" by Nagao et al. Detailed studies about division number, Monte Carlo active space, magnetic field, temperature and distance dependences were performed in order to clarified the scope and limitation.

INTRODUCTION

The path integral introduced by Feynmann[1, 2] has been applied to many problems[3-7] in quantum mechanics. Recently, we presented the path integral formulation[8] based on a molecular orbital picture by means of the Thouless parametrization. It was applied to the studies of magnetic properties such as the magnetization. In our treatment the *ab initio* Hamiltonian and the Zeeman Hamiltonian were used. Numerical calculations were performed with the Monte Carlo (MC) method[8, 9]. This method can calculate exact magnetic properties including temperature effects as infinite MC steps.

In this paper this method is applied to the simple system of a methyl and hydrogen radical pair system as a extended model from studying the hydrogen molecule in the series paper entitled "part I" by Nagao et al.[10] In this system the magnetic interaction between s-orbital and p-orbital can be take into account, though they had successfully applied the path integral procedure to the system between s-orbitals and derived interesting physical properties. These results obtained by this method seems to clarified the scope and limitation.

It is difficult to carry out the calculations which are involved many electron excitations because of needing very long running time. Therefore, we modified the our program to deal with only important electrons, that is, limit excitation spaces of electrons.

This treatment is similar to the complete active space (CAS) in the *ab initio* MO calculation methods. The dependence on the number of division with respect to the partition function is discussed. The characters and the physical properties under various situations as to temperatures and external magnetic fields are also examined.

THEORETICAL BACKGROUND AND CALCULATION SCHEME

In our treatment temperature effects are obtained by calculating the partition function $Z = Tre^{-\beta H}$. Here, Hamiltonian consists of the *ab initio* Hamiltonian and the Zeeman Hamiltonian. According to the path integral method the term $e^{-\beta H}$ can be divided into N parts, that is the division number is N. A path integral representation is derived by inserting the closure relations. Partition functions are calculated in each Monte Carlo steps by the Metropolis method[11]. Random numbers generated with maximum length linearly recurring sequence[12]. In order to avoid the negative sign problem a reweighting method is attempted. Finally, the ensemble average of the total energy and the magnetization (1) etc. are obtained by the above procedure.

$$\langle M_z \rangle = \frac{Tr\left[e^{-\beta H} M_z\right]}{Tr\left[e^{-\beta H}\right]} \tag{1}$$

According to the series paper entitled "part I", the initial coherent state is constructed by the natural orbitals (NO) based on the Hartree Fock (HF) calculation. We employed the 4-31G basis sets. For this purpose GAUSSIAN 94 program package[13] on the IBM RS/6000 work stations was used. Two electron integrals were generated by means of HONDO 95.3 program package[14].

NUMERICAL CALCULATIONS

In order to examine the performance of this method we treated a system which consists of both methyl radical and hydrogen atom in relation to the system between hydrogen atoms in the previous part I. Figure 1 illustrates the model system under consideration. The axis of magnetic field was set as z-axis. The through space length between these two radicals was indicated as R/Å and our calculations were progressed at fixed 2.0Å at first.

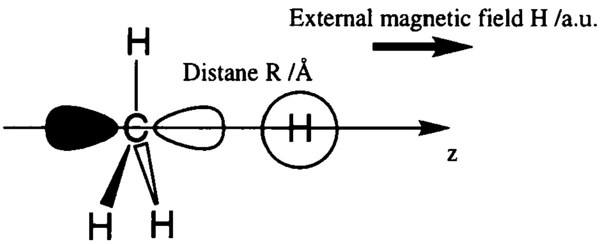


FIGURE 1 Employed model consists of methyl and hydrogen radicals

Calculation about only SOMO-SOMO MC-AS

Here, the magnetic interaction between radical pairs was considered under the limitation of Monte Carlo Active Space (AS), that is, (α-hole, α-particle, β-hole, β-particle space)=(1, 1, 1, 1). Such limitation is found to be correspond to that in the paper of part I, indicating the necessity of only SOMO-SOMO direct interaction. At first, we investigated the dependences of the ensemble average of the total energy and the magnetization on the division number for the partition function. These calculations were carried out under conditions that temperature T is 1K and external magnetic field H is 0 or 1 a.u. (1 a.u. =

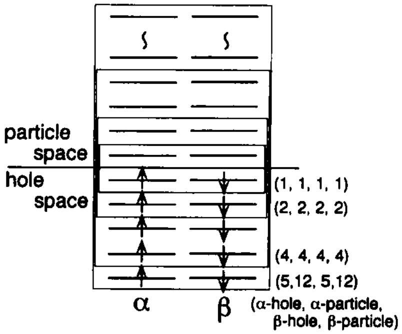
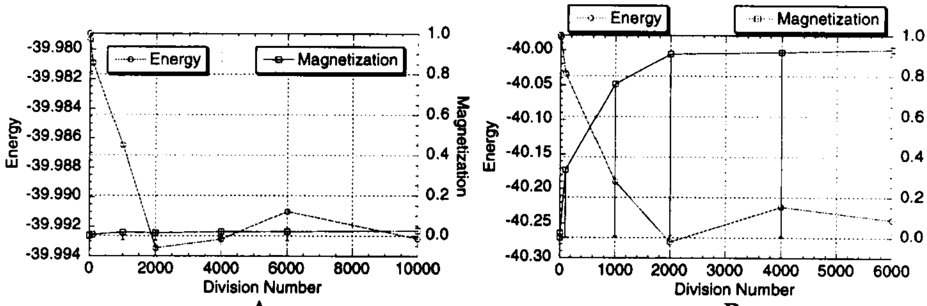


FIGURE 2 Definitions of Active Space (AS)



A B

FIGURE 3 Total energy for the number of division at T=1K.
Here fig A and B indicate results at H=0 and 1 a.u., respectively.

2.3506×10^5T). Figures 3A and B show these results, respectively.

As increasing the division number, it is noteworthy that the total energy become more stable because of including more electronic correlations. However, we could not find remarkable improvements in the region which is larger than N=4000. The more huge number of divisions are desired in order to include more correlations, though it is very time consuming as increasing the number.

In order to contrast these above results, *ab initio* MO calculations were carried out by *ab initio* HF, post-HF and UNO CAS calculations. Here, we also employed the 4-31G basis sets. The energy of low spin state with RHF(based on UNO) was -39.978868020861 a.u. On the other hand, Coupled-Cluster method (RCCSD(T)) which the most involved electron correlations in these methods gave -40.143976717 a.u. The calculated J_{ab} values by APUHF, APUCC(T) and UNO CASCI{2,2} method were -7262.88, -11766.7 and -7969.66 cm^{-1}, respectively.

Expanding MC-AS

In the previous section, we performed the calculations based on the path integral method about only the limited AS (1, 1, 1, 1). Here let us investigate the dependence on the AS.

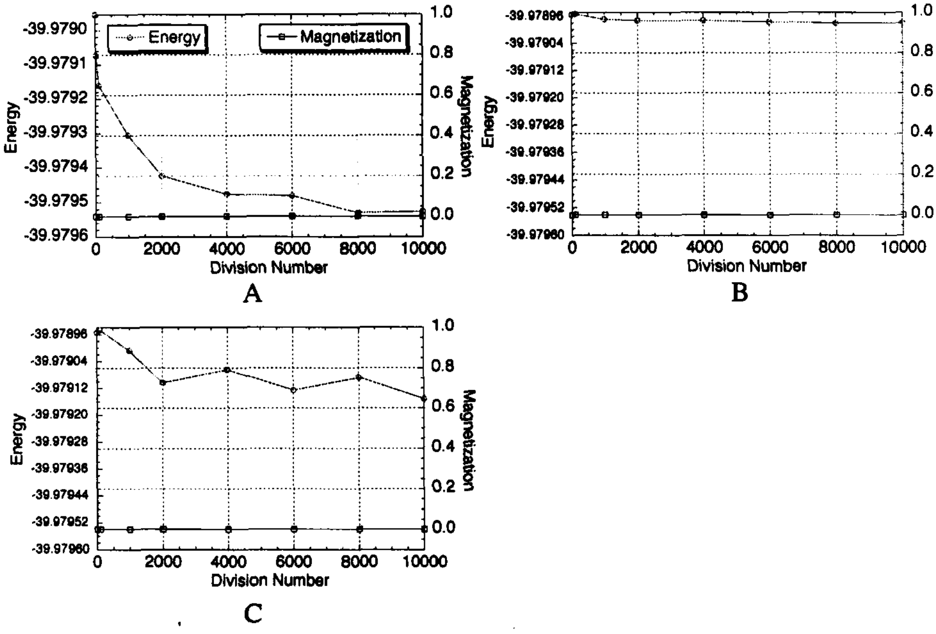


FIGURE 4 Total energy for the number of division at T=1K.
Here fig A, B and C indicate results at AC(2, 2, 2, 2), (4, 4, 4, 4) and (5, 12, 5, 12), respectively.

Judging from UNO analysis, it is found that the suitable MC-AS are (2, 2, 2, 2), (4, 4, 4, 4) and (5, 12, 5, 12). The latest AS is correspond to involving all orbitals. As the program coded by our group can calculate in also any Monte Calro Active Spaces, calculations with these ASs were also performed. Figures 4A, B and C depict the total energies and the magnetizations for each AS at same conditions which temperature T is 1K, the division number N is 1000 and the external magnetic field H is 1 a.u.

From these figures, it is noteworthy that curvature of the total energies vs the division number have same tendency, that is, as increasing the division number, the total energy will decrease up to the exact total energy obtained from the calculation by *ab initio* Full-CI method at the temperature of 0 K. The dependency on the ASs is found that the few damping of the total energy could not be taken in the case of the wider ASs. In such the case, huge number of steps is required because of many integral variables. Thus, it is important to consider the valance of the AS and N. On the other hand, it is expected that more significant results involved all contributions may be given in such the case, since more indirect correlations can be involved.

Unfortunately, we could not investigate the detailed contributions from magnetic interactions for the lack of sufficient available CPU time. We are carrying out the more accurate calculations for this purpose now. However, we can conclude that the only SOMO-SOMO interaction i.e. AS (1, 1, 1, 1) plays the dominant role to magnetic behaviors between methyl-hydrogen radicals as first step of approximation. Therefore, we employed this simplest and narrowest AS in following sections.

Dependences on magnetic field

As the discussed previous sections, availability of the our scheme for studies about the total energy and the magnetization were ensured. Here, let us study the dependence on the

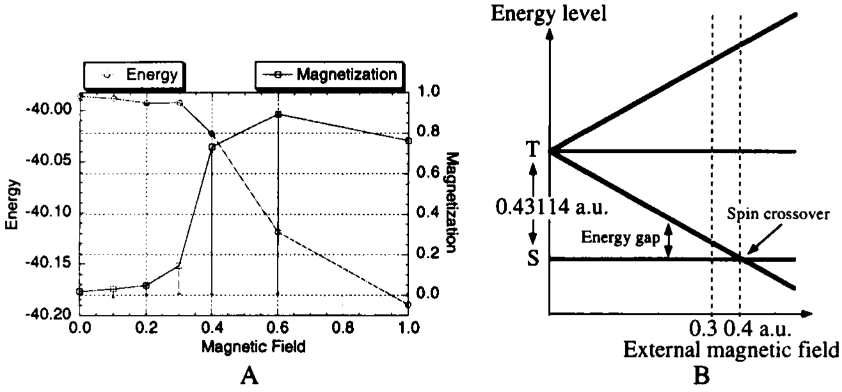


FIGURE 5 (A) Magnetization for various external magnetic field at T=1K.
(B) Energy splitting diagram impressed magnetic field

external magnetic fields. In relation to such a strong magnetic field, recently it is proposed that more interesting sciences which cannot be expected under traditional week magnetic field.[15] Many empirical and theoretical studies are anticipated by a lot of scientists. The total energy and the magnetization for each external magnetic field from 0 to 1 a.u. are depicted in fig. 5A. These calculation was performed under a condition that N=1000 and T=1K, though much larger N was desired as discussed the previous sections.

From fig. 5A, it is found that the magnetization curvature increases drastically at H= 0.3 ~ 0.5 a.u. region. In order to analyze the result, let us investigate the behavior of triple and singlet state under various external magnetic fields. In fig. 5B, the energy splitting diagram is illustrated. From fig. 5B the relation between magnitude of external magnetic field and triple-singlet energy gap is drawn and this figure help to describe the behaviors under various magnetic fields. The result indicates that spin crossover is occurred in this region and the transition with the spin flop from singlet state to triple state. The situation is the same in the case of hydrogen molecule studied by Nagao et al.

<u>Dependences on temperature</u>

Here, we progressed the calculation at nearly spin crossover region (H=0.3a.u). Figure 6 shows the results in various temperatures.

The temperature will be equivalent to the energy gap between singlet state and triplet state, as illustrated in fig. 5B. In this calculation, it seems that the critical temperature can be detected and spread widely. On the other hand, in a region of the higher temperature of 4000K, the two states are mixed each other with excessive heat energy and the magnetization is vanished. The tendencies concluded for this system was also reported in the case of hydrogen molecule.

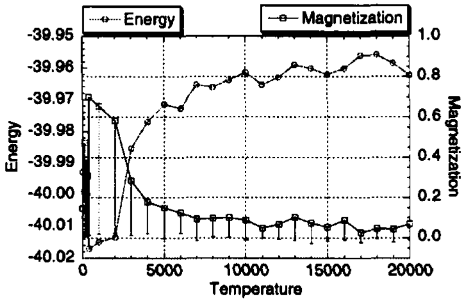


FIGURE 6 Magnetization for various temperature at H=0.3 a.u.

Dependences on the distance between radical pairs

In the above sections, the fixed inter radical distance (R=2.0Å) was employed and our treatment was applied for the strong interaction system such as large J_{ab} values. In such system HOMO-LUMO gap is much larger because of direct interaction between SOMOs of each radicals as shown in table I. Here, we carried out calculations based on path integral method at a few distance R = 1.0, 2.0, 3.0 and 4.0Å in order to clarify its feature about various interaction from large gap limits to nearly degenerate limits. Figure 7 depicts the calculated results.

From the fig. 7 the magnetizations between at 1.0 and 2.0 a.u. etc. have distinct difference. These results are found to be consistent with our idea, that is, the spin crossover is occurred as relation to the S-T gap shown in fig. 5.

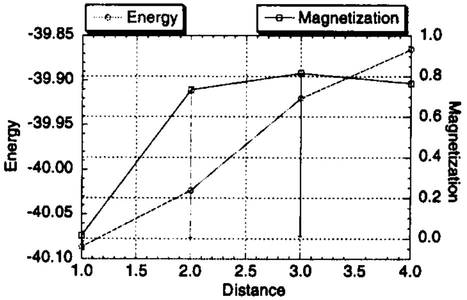


FIGURE 7 Magnetization for various inter-radical distance R /Å at T=1 K and H=1 a.u.

CONCLUSION REMARKS

On calculating these values of the ensemble average of physical properties, we could not take a great number of divisions. So the numerical accuracy might not be sufficient, but we expect that this method was effective to calculate magnetic properties in qualitative discussions. We presented successfully the theoretical treatment based on a path integral methods. It is noteworthy that path integral method could be developed and applied to calculation of magnetic properties in real molecular system. These programs were developing at our group and we plan to deal with interesting and complex systems such as the organic-metal conjugated system with dπ-pπ bond. We also expect to gave powerful tool to study the phenomena under strong magnetic field. More detailed calculations in such systems are carrying out now.

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