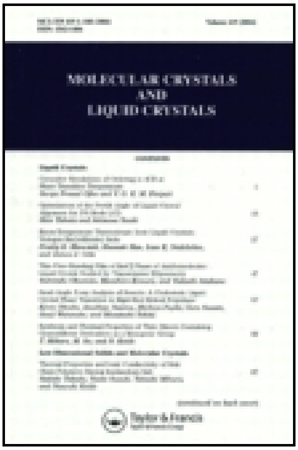

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CALCULATION OF MAGNETIZATION BY PATH INTEGRAL METHOD I.

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Abstract The path integral method is formulated by means of the extended Thouless parametrization. The *ab initio* Hamiltonian and the Zeeman Hamiltonian are used in our model systems. Numerical calculation of physical properties of molecules is performed in terms of the Monte Carlo method. The dependence of the magnetization of a hydrogen molecule on the division for the partition function, the temperature and the external magnetic field is discussed.

INTRODUCTION

The path integral was first introduced by Feynman[1,2] and has been successfully applied to many problems[3-7] in quantum mechanics. The path integral method has applied to the many-electron systems in quantum chemistry[8,9]. Recently, we have presented a path integral formulation in terms of the LCAO coefficients[10]. Because the path integral is expressed as multi-dimensional integrals with a huge number of variables, we cannot directly compute this integration by ordinary ways. Therefore, we use a statistical method such as the Monte Carlo method[11,12]. In this paper, we present the path integral method by means of the extended Thouless parameterization for dealing with spin flop phenomena and examine numerical calculations of the magnetization by the Monte Carlo method. In particular, the magnetization value of the antiferromagnetic materials in strong magnetic field will be shown.

THEORY AND NUMERICAL SCHEME

We briefly mention our path integral formulation by means of the extended Thouless parametrization. Our numerical scheme for calculating the magnetization by Monte Carlo method is presented.

General Theory

Let $|\phi\rangle$ be a Slater determinant composed of N orbitals (hole-orbitals):

$$|\phi\rangle = \prod_{\sigma=\alpha,\beta}\prod_{h=1}^{N_\sigma} a_{h\sigma}^{+}|0\rangle \quad , \tag{1}$$

where N_σ means the number of hole-orbitals with spin σ, and $N = N_\alpha + N_\beta$. Slater determinant $|Z\rangle$ is written in terms of complex coefficients $Z_{ph}^{\rho\sigma}$ as

$$|Z\rangle = \det\left(1 + Z^{+}Z\right)^{-\frac{1}{2}} \exp\left[\sum_{\substack{\sigma=\alpha,\beta\\ \rho=\alpha,\beta}}\sum_{p=1}^{M-N_\rho}\sum_{h=1}^{N_\sigma} Z_{ph}^{\rho\sigma} a_{p\rho}^{+} a_{h\sigma}\right]|\phi\rangle \tag{2}$$

$$= \det\left(1 + Z^{+}Z\right)^{-\frac{1}{2}} \prod_{\substack{\sigma=\alpha,\beta\\ \rho=\alpha,\beta}}\prod_{h=1}^{N_\sigma}\left(a_{h\sigma}^{+} + \sum_{p=1}^{M-N_\rho} Z_{ph}^{\rho\sigma} a_{p\rho}^{+}\right)|0\rangle \quad , \tag{3}$$

where M is the number of the base. The p labels denote the particle orbitals that orthogonal to the hole orbitals h, and Z is a matrix whose elements are $Z_{ph}^{\rho\sigma}$. The Slater determinant (3), which is a expression of Thouless parametrization, may be considered to be an expression of generalized coherent state. The closure relation may be constructed.

According to the traditional path integral method, we divide $e^{-\beta H}$ into n factors. By inserting the closure relation between each factor, a discretized path integral representation of the partition function is derived.

We use the following Hamiltonian for the present path integral representation:

$$H = \sum_{\sigma=\alpha,\beta}\sum_{i,j=1}^{M} h_{ij}^{\sigma} a_{i\sigma}^{+} a_{j\sigma} + \frac{1}{2}\sum_{\sigma,\rho=\alpha,\beta}\sum_{i,j,k,l=1}^{M} V_{ijkl}^{\sigma\rho\rho\sigma} a_{i\sigma}^{+} a_{j\rho}^{+} a_{k\rho} a_{l\sigma} - 2\mu_0 \mathrm{H}_0 \sum_{i=1}^{M} S_{iz} \quad . \tag{4}$$

The first and second terms in the right hand mean the *ab initio* Hamiltonian, and the third term is the Zeeman Hamiltonian. The matrix elements of the total Hamiltonian

H for the coherent states $|Z\rangle$ are easily derived analytically.

Scheme

To calculate the ensemble average of physical properties such as the energy, the magnetization, we need the matrix elements, h_{ij}^{σ} and $V_{ijkl}^{\sigma\rho\rho\sigma}$, between orbitals in each term of eq.(4). Because our initial coherent state is constructed by the Hartree-Fock(HF) orbitals, matrix elements based on the HF orbitals must be generated. From HF calculations by means of HONDO95 program package[13], the HF natural orbitals and the molecular integrals based on the basis set are obtained. We convert them into the molecular integrals based on the HF orbitals.

Using the matrix elements, h_{ij}^{σ} and $V_{ijkl}^{\sigma\rho\rho\sigma}$, obtained from above procedure and the discretized path integral representation, we calculate the ensemble average of the energy,

$$\langle H\rangle = \frac{Tr\left[e^{-\beta H}H\right]}{Tr\left[e^{-\beta H}\right]} \quad , \qquad (5)$$

by the Monte Carlo method. The ensemble average of the magnetization $\langle M_z\rangle$ is also computed as the same procedure.

NUMERICAL EXAMPLES

As an numerical example, first, the total energy of a hydrogen molecule is calculated. We compare the results with those obtained from the conventional molecular orbital theory. Next, we show the calculation results of the magnetization $\langle M_z\rangle$ of the hydrogen molecule. Here, the dependence of the $\langle M_z\rangle$ value on the number of the division for the partition function, the temperature and the external magnetic field is discussed.

Total Energy Of Hydrogen Molecule

We consider a hydrogen molecule with an atomic distance of 1.46 a.u.. All calculations were carried out under a 4-31G basis sets. Figure 1 shows the total energy vs the number of the division for the partition function at the temperature of 1K. For 10^4 divisions, the total energy becomes -1.138332844±0.001118242 a.u.. The full-CI total energy obtained by HONDO95 is -1.151271902 a.u.. We can expect that when the number of division becomes large, the total energy will be equal to that of full CI.

The total energy for each temperature is shown in fig.2. The present calculation was performed under a condition of the division number N of 1000 and without magnetic field. In the region higher than the temperature of 300 K, when the temperature becomes high, the total energy also increases as expected. On the other hand, the above tendency is not found in the region under 300K. The reason is that the electron correlation is not sufficiently included especially for the temperature under about 200 K, because the division number *N* of 1000 is too small. However, we may obtain the tendency of the dependence of physical properties on the temperature qualitatively.

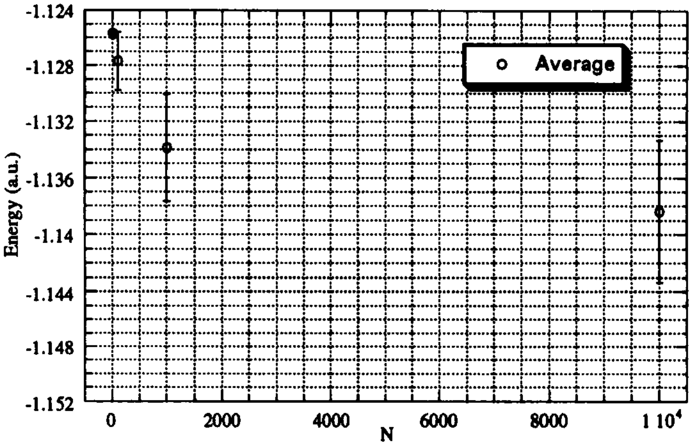

Figure 1. Total energy for the number of division.

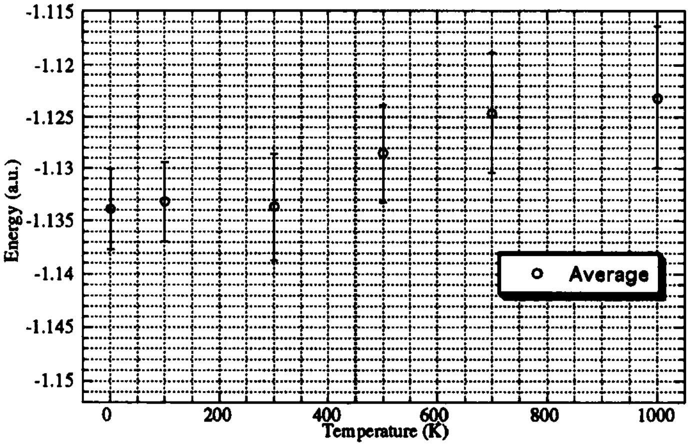

Figure 2. Total energy vs temperature.

Magnetization Of Hydrogen Molecule

Next, we calculate the magnetization and show the dependence on the external magnetic field and the temperature. Figure 3 depicts the magnetization for each external magnetic field at the temperature of 1K, where N is 1000. Here, note that one magnetic field atomic unit corresponds to 2.3506×10^5 T. We can classify the intensity of the magnetic field into three regions according to the behaviour of the magnetization. In the first region less than the magnetic field of 0.5 a.u., the spin state of the molecule is antiferromagnetic. In the second region from 0.5 a.u. to 1.5 a.u., the spin flop happens. In the third region larger than 1.5 a.u., the spin state becomes paramagnetic.

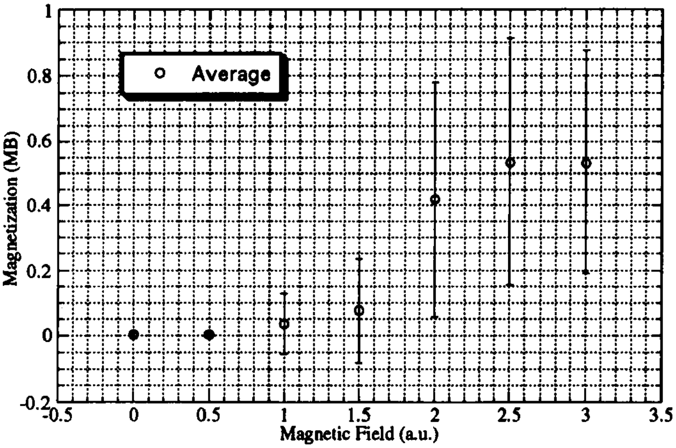

Figure 3. Magnetization vs magnetic field.

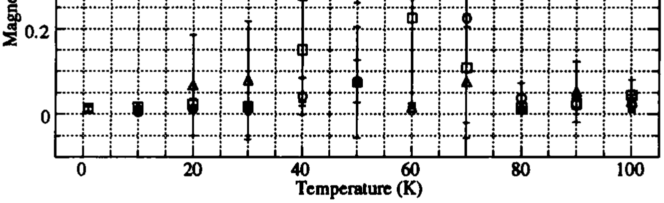

Figure 4. Magnetization vs temperature.

The magnetization for each temperature is shown in fig. 4. A peak of the magnetization for the magnetic field of 1.0 a.u. is found at the temperature of 50 K. For the magnetic field of 0.95 a.u., the peak shifts to a temperature lower than 50K.

On the other hand, the peak shifts to a higher temperature for the magnetic field of 1.05 a.u.. The peak at the low temperature occurs for the magnetic field inducing the spin flop.

CONCLUDING REMARKS

We present a path integral formulation by extended Thouless parametrization and a computational scheme to calculate the ensemble average of magnetization. We show the magnetization value of the antiferromagnetic materials in strong magnetic field. In such a field, there are several interesting phenomena which is a chemical catastrophe and so on. Our method may be a powerful tool to investigate such phenomena. In our next step, our scheme must be reformed to yield more quantitative results.

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REFERENCES

1. R.P.Feynman, Rev.Mod.Phys., 20,367(1948)
2. R.P.Feynman, Phys.Rev., 76,769(1949); ibid 80,40(1950)
3. J.P.Blaizot and H.Orland, Phys.Rev., 24,1740(1981)
4. R.P.Feynman and A.R.Hibbs, Quantum Mechanics and Path Integrals (McGraw-Hill Book Company, New York, 1965)
5. L.H.Ryder, Quantum Field Theory (Cambridge University Press, London, 1984)
6. J.W.Negele and H.Orland, Quantum Many-Particle Systems(Addison-Wesley Publishing Company, 1988)
7. J-P.Blaizot and G.Ripka, Quantum Theory of Finite Systems (Massachusetts Institute of Technology, 1986)
8. H.Nagao, K.Nishikawa and S.Aono, Chem.Phys.Lett., 190,97(1992); ibid., 215,5(1993)
9. H.Kawabe, K.Nishikawa and S.Aono, Int.J.Quantum Chem., 51,265(1994)
10. H.Kawabe, H.Nagao and K.Nishikawa, to be published in Int.J.Quantum Chem.
11. H.Kawabe, H.Nagao and K.Nishikawa, to be published in Int.J.Quantum Chem.
12. M.Suzuki ed., Quantum Monte Carlo Method in Condensed Matter Physics (World Scientific Publishing Co. Pte. Ltd., Singapore, 1993)
13. M.Dupuis, A. Marquez, and E. R. Davidson, "HONDO 95.3 from CHEM-Station", (1995) IBM Corporation, Neighborhood Road, Kingston, NY. 12401.