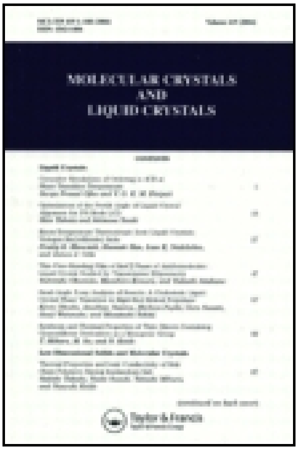

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# Generalized Spin-Density Functional Calculation for the Spin Frustrated Systems

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# Generalized Spin-Density Functional Calculation for the Spin Frustrated Systems

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We developed the *ab initio* Linear Combination of Gaussian Type Orbital (LCGTO) program with generalized Hartree-Fock-Slater functional and calculate the hydrogen cluster as models of the noncollinear systems. Calculational results are compared with that of *ab initio* GHF and the difference between them are discussed.

*Keywords:* noncollinear molecular-magnetism; localized spin density approximation; generalized Hartree Fock

## 1 Introduction

In the last decade the physics and the chemistry of single-molecular-magnetism have attracted much interest. The numerous nanoscale clusters such as $Mn_{12}$ac, $V_{15}O_{42}$ etc. have been synthesized and analyzed[1]~[3]. Although the fundamental parameter of their appealing phenomenon such as the magnetic hysteresis and the quantum tunneling is the anisotropic magnetic moment, little is known about the intramolecular spin structure. Recently, Z.Zeng et.al implemented the discrete variational - localized spin density approximation ( LSDA ) calculations for $Mn_{12}$ and $Fe_{11}$. They pointed out the possibility of the intramolecular spin-frustration by determining the intramolecular effective exchange integrals, but could not pursue it further since they use the collinear LSDA[3]. Previously, we have discussed torsional spin structure in $Mn_{12}$ Ac and other species on the basis of the classical Heisenberg ( CHB ) model by using their observed effective exchange integrals [4]. Many of the nanoscale clusters is expected to exhibit noncollinear magnetism since they include the spin frustrated parts, which are enumerated in our previous paper, in their metal skeleton. Practically, magnetic measurements of vanadium oxide cluster ( $V_{15}O_{42}$ ) have shown a noncollinear spin alignment in the ground state [2].

To research noncollinear molecular-magnetism computationally, we have developed the ab initio Linear Combination of Gaussian Type Orbital (LCGTO) LSDA program. To our knowledge, the present study is the first application of the ab initio LCGTO method of the generalized spin DFT to the molecule.

## 2 Theoretical background

### 2. 1 Local spin density approximation for noncollinear systems

To construct the noncollinear LSDA functional, all we need is the following replacement of the fundamental parameters.

$$E_{xc}[\rho_\alpha,\rho_\beta] \rightarrow E_{xc}[n,\vec{\zeta}] = \int d\mathbf{r}n(\mathbf{r})\varepsilon(n(\mathbf{r}),\zeta(\mathbf{r})) \qquad (1)$$

The exchange functional at the left side is for collinear systems. The $\rho_\alpha$ and $\rho_\beta$ are α and β spin densities respectively and therefore this functional does not depend on the off-diagonal terms of the spin density matrix. The exchange functional form at the right side is for the noncollinear systems. The fundamental parameters are the number operator $n$ and the spin polarizability $\zeta$. Note that $\zeta$ is not equal to $(\rho_\alpha - \rho_\beta)/n$ in general,but equal to $|Tr\sigma \cdot \rho|/n$, where $\sigma$ is the vector of the Pauli matrix, $(\sigma_x,\sigma_y,\sigma_z)$, and $\rho$ is the 2×2 spin density matrix, so that the exchange functional depend on the off-diagonal terms of $\rho$. This is equivalent to the original form of LSDA functional proposed by von Barth and Hedin[5]. It is important to note that there is a essential difference in the exchange term between the noncollinear LSDA and GHF. The exchange term in the former method depends only on the up- and down- spin densities which are defined locally due to the localized spin approximation, while that in the latter method depends on the all four terms of the 2×2 spin density matrix[6]. Then we focused on the application of LSDA to the molecular system and its comparison with that of GHF.

### 2. 2 Computation and the type of solutions

The Kohn-Sham orbitals for the noncollinear systems are expressed by the spinors as are the GHF molecular orbitals so the equation for the noncollinear LSDA is the coupled equation for the general spin orbitals. The exchange terms of LCGTO-DFT was evaluated numerically by using the Becke fuzzy scheme[7]. We used the Hartree-Fock-Slater (HFS) functional[8] and 3-21G basis set in the following calculations.

As to the analyses of the solutions, the classification of the GHF solutions by H.Fukutome[6] and magnetic group theory[9] are powerful tools as in the case of the CHB model [4]. The collinear magnetic solution of the molecular system correspond to the Axial Spin Density Wave ( ASDW ) in the eight types. Helical Spin Density Wave ( HSDW ), which were referred to as Torsional Spin Density Wave ( TSDW ) in his original paper , and Torsional Spin Density Wave ( TSW ) are noncollinear magnetic solutions with two dimensional (2D) and three dimensional (3D) spin modulations, respectively. Other types of GHF solutions are not spin-polarized, so we do not describe them here. He also provide the theory of the instability analysis of the GHF solutions[10]. His formulation in these series of papers, except the implicit form of the instability matrix, as well as the magnetic group theory, does not depend on the exchange potential terms of the GHF equations so that these theories can apply to generalized DFT solutions directly. Thus we applied these theory for interpretation of the computational results.

## 3 Triangular spin alignments

Due to limitations of space, we only present the results of a triangle three hydrogen ($H_3$) system, illustrated by Fig.1. We performed generalized HFS ( GHFS ) and GHF calculations for the each geometries in ( $R_1$ , $R_2$ ) space. The energy gap of the ASDW solution and the HSDW solution at each point by GHFS and GHF are plotted in Fig. 2 (A) and (B),respectively. The black region corresponds to

Fig.1 Schematic illustrations of the cluster models and its parameters for a triangle hydrogen system ( $C_{2v}$ symmetry )

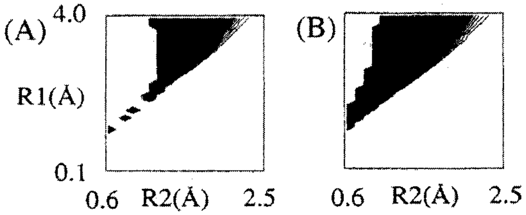

FIGURE 2 The sign of E(HSDW)-E(ASDW) in ( R1 , R2 ) space. The meaning of black and white regions is given in the text. (A) GHFS ; (B) GHF.

negative E(HSDW)-E(ASDW) indicating that HSDW is the ground configuration. The discontinuous region in small ( $R_1$ , $R_2$ ) in GHFS is due to the difficulty of SCF convergence. The region for both GHF and GHFS solutions are divided into three regions by the instability boundaries of the ASDW solutions as shown in Fig.3. The spin density of GHFS solutions in the Region I,II,III are shown in Fig.4(A),(B),(C), respectively. From these plots, the region I is found to be regarded as a hydrogen atom with a nearly non-magnetic hydrogen molecule. The solutions in this area is categorized in ASDW solutions, which we call $ASDW_1$. The region II are characterized as the HSDW region at which the spin-frustrations of the triangular radicals occur. The solutions in the region III is the typical ASDW solutions ,which we denote $ASDW_2$, as illustrated in Fig.4(C).

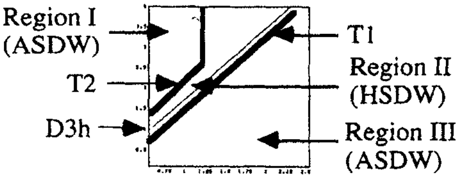

FIGURE 3 The schematic illustrations of the instability boundaries of the ASDW solutions in ( R1 R2 ) space. See text for characterizations of the regions and boundaries.

The boundary $T_1$ between the region II and region III is that of A.M instability[10] which brings about the noncollinearity of the magnetism. We see from Fig.2(A) and (B) that the line of A.M instability threshold of the GHFS solutions is close to that of GHF solutions. This indicate that there are little difference between the GHF and GHFS methods in the description of the noncollinearity emerging from A.M instability . On the other hand, the situation is more complicated in the boundary $T_2$. It is apparent from Fig.2(A) and (B) that the instability line $T_2$ of the GHFS shifts to large $R_2$ side in compared with that of GHF. To explain this difference, we must discuss the interconnection relation between the $ASDW_1$ and HSDW[11]. The HSDW does not emerge from A.M instability of the $ASDW_1$ directly. At first, he $ASDW_1$ is $A_+M_+$ unstable at the neighborhood to $T_2$ and the $C_{2v}$ symmetry-forbidden ASDW,which we call $ASDW_3$, emerge from this $A_+M_+$ instability. Furthermore, A.M instability occurs at a boundary which is very close to the preceding instability boundary. Therefore we cannot show the $ASDW_3$ stable region. The way of this interconnection of $ASDW_1$ and HSDW is illustrated in Fig.5 together with that of $ASDW_2$ and HSDW. Since, as described above, the $ASDW_1$ can be regarded as a hydrogen atom with a nearly non-magnetic hydrogen molecule, the $A_+M_+$ instability can be interpreted, roughly speaking, as the $^3ST_-$ instability of the hydrogen molecule. Thus the shift of the instability line $T_2$ of GHFS is attributable to the intrinsic nature of collinear LSDA[12] .

It is noteworthy , as shown in Fig.6, that the spin density at each site of the equilateral triangle $H_3$ ($D_{3h}$ ) of the GHFS more rapidly converges the value in the infinite limit of the interatomic distance than that of the GHF. This result imply that for the noncollinear magnetic systems, GHFS underestimate the magnetization, as well as for collinear magnetic systems in the intermediate region[12].

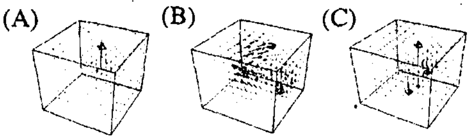

FIGURE 4 The spin density plots of GHFS solutions of (A) Region I, (B) Region II, and (C) Region III, respectively.

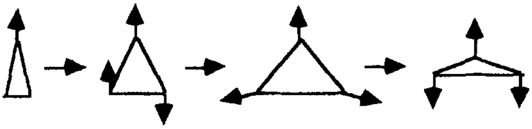

FIGURE 5 The way of the interconnection of ASDW1 and ASDW2 solutions through HSDW state

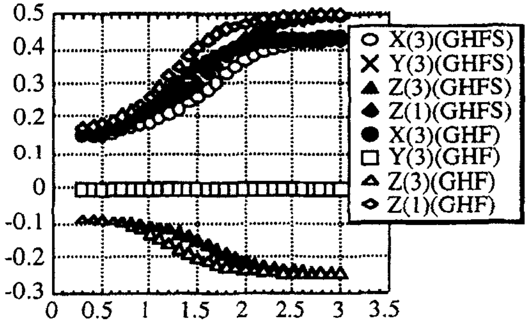

FIGURE 6 The spin densities of the equilateral triangle H3 (D3h ) at each site by GHFS and GHF

## 4 Concluding Remarks

We have developed the LCGTO program of the generalized LSDA method and investigated for model clusters with noncollinear spin alignments. Comparison of GHF and GHFS for the simple example gave the good agreement in the $A_-M$ instability point of the ASDW solution. On the other hand, there are differences in describing the $A_+M_+$ instability of and estimating the magnetization, which can be ascribed to that between UHF and UHFS.

From these results, generalized LSDA is found to be useful for understanding the spin correlation in the noncollinear molecular magnetism as in the case of the collinear magnetism. We expect that these approaches give some insight in the intramolecular spin structure in the nanoscale clusters.

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