

# Development of efficient quantum chemical methods for designing organic ferromagnets

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(有機強磁性体設計のための効率的量子化学手法の開発)

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### 論 文 内 容 の 要 旨

Design and preparation of organic ferromagnets are very important from both experimental and theoretical viewpoints. Predicting the high spin stability of organic radicals correctly for designing organic ferromagnets remains a significant challenge. The application of conventional ab initio methods to huge high spin open-shell systems faces difficulties because of a rapid increase in CPU time as the size of the system increases. In this thesis, some efficient quantum chemical methods were developed for designing organic ferromagnets.

The open-shell elongation method developed in this thesis and tested on the polyglycine radical, nonbonding allyl radicals, and polyethylene radical can reproduce the results of conventional method. (i.e., differences in energy per atom between the open-shell elongation method and conventional method can be very small ( $\sim 10^{-10}$  a.u. per atom)). This method with cutoff technique can be linear scaling and very accurate for performing electronic structure calculations of huge open-shell systems.

A method with an index ( $L_{\min}$ ), called  $L_{\min}$  method, was developed at the restricted open-shell Hartree–Fock (ROHF) level for predicting the high spin ground state stability of conjugated organic radicals. A localization method, called minimized mixing molecular orbital (MMMO) localization method, was developed for localizing the coefficients of nonbonding molecular orbitals (NBMOs), and subsequently the localized coefficients were used to calculate  $L_{\min}$  that indicates the high spin stability of conjugated organic radicals. The MMO localization method was combined with the open-shell elongation method at the ROHF level, called minimized mixing elongation (MMELG) method. The  $L_{\min}$  method can be combined with the MMELG method to treat huge high spin open-shell systems. Thus, it was demonstrated that the  $L_{\min}$  method and the MMELG method are useful for

designing organic ferromagnets.

The polarizable continuum model (PCM) was combined with the MMELG method for accurate and efficient electronic structure calculations of the lowest and highest spin states of huge open-shell systems with solvent effects. This MMELG-PCM method was also combined with the  $L_{\min}$  method to show the high spin stability of huge organic polyradicals (MMELG-PCM- $L_{\min}$  method). It was proved that the MMELG-PCM- $L_{\min}$  method can be efficiently and reliably applied to predict the high spin stability of organic polyradicals and thus useful for designing organic ferromagnets with solvent effects.

A method with index  $L_{AP}$ , by means of “Analytical Prediction” method, was developed for predicting high spin stability of alternant conjugated hydrocarbon polyradicals without ab initio calculations. The formulas of  $L_{AP}$  were derived analytically as the function of the number of unpaired electrons, denoted as  $N$ , without performing any localization procedure to attain the minimum mixing between NBMOs. The relationship between the  $L_{AP}$  method and high spin stability was confirmed by investigating some high spin open-shell systems. It was shown that this approach can be a useful tool for designing organic ferromagnets.

As an another analytical approach, a molecular fragment interaction (MFI) method was also developed for predicting the high spin stability of alternant and non-alternant conjugated hydrocarbon radicals without ab initio calculations. The MFI method comprises three steps: (1) division of the system into fragments and numbering of the carbon atoms, (2) construction of a secular equation, and (3) solving of the secular equation. If there are two or more NBMOs and the smallest number of bonds between two carbon atoms with unpaired electrons is an even number, then the conjugated hydrocarbon radical has a high spin ground state. This method can also be used to compare the high spin ground state stability between different conjugated hydrocarbon radicals. If a conjugated hydrocarbon radical has a high spin ground state, then its derivative has a high spin ground state as long as the degeneracy of the NBMOs is kept. It was suggested that this analytical treatment is also useful for the rapid design of organic ferromagnets.