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開殻高分子安定スピン状態予測のための非結合性
最小 Mixing (NB-MM) MO-ELG 法

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NB-MMMO method for the prediction of the spin state stability
in open-shell polymer systems

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1. Introduction

Organic ferromagnets have attracted much attention during the last decades [1-3]. Predicting the high spin stability of conjugated organic radicals correctly is very important for the design of organic ferromagnets. However, the correct calculation of $\Delta E(L - H)$ that is the energy difference between the lowest and highest spin states is still very difficult. In this work, we used the Non-bonding minimized mixing (NB-MM) MO-ELG- L_{\min} method to study the high spin stability of huge open-shell polymers for designing organic ferromagnets.

2. Method

2.1. The NB-MMMO-ELG method

Suppose that a system has N units and each unit has an unpaired electron with up spin (see Figure 1). The eigenvalue problem is solved for the starting cluster $A + B$ part. Canonical molecular orbitals (CMOs) of the starting cluster are localized into A_1 part and B part. Next, the eigenvalue problem of $B + M$ part is solved. After that, the CMOs of the $B + M$ part are localized into A_2 part and B part. The procedure is repeated until the whole system is calculated.

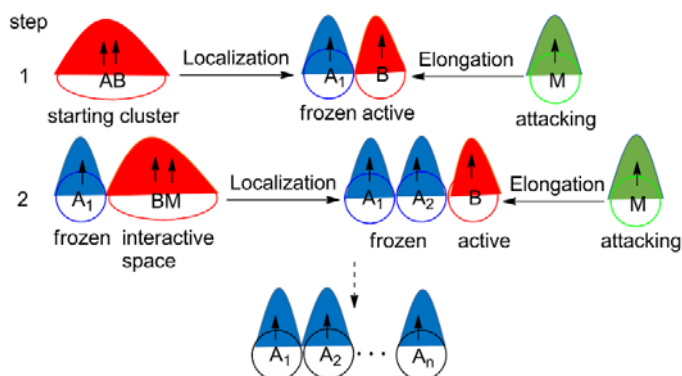


Figure 1 Flowchart of the NB-MMMO-ELG method

2.2. The L_{\min} method

As calculating $\Delta E(L - H)$ correctly is still very challenging, a method with index L_{\min} was developed for efficient design of organic ferromagnets [1, 2]. Unitary transformation is performed iteratively on the coefficients of nonbonding molecular orbitals (NBMOs) generated by the NB-MMMO-ELG method. Process of unitary transformation for many NBMOs can be found in Ref. [2]. The index L_{\min} is defined as the minimized mixing between NBMOs and calculated as $L_{\min} = \sum_{j>i} \sum_r C_{ri}^2 C_{rj}^2$. Once the value of L_{\min} is obtained, it can be used to predict the high spin stability of conjugated organic radicals.

3. Results and discussion

In Figure 2, model 1 was obtained from polymer 1 in Ref. [3] by replacing the tert-butylbenzene group with hydrogen; subsequently, model 2 was obtained from model 1 by replacing two carbon atoms with two silicon atoms. Parts of models 1 and 2 were optimized at the level of

UB3LYP/6-31G(d); after that, the optimized parts were used to construct the whole system for calculations of L_{\min} and $\Delta E(L-H)$. As shown in Table 1, L_{\min} and $\Delta E(L-H)$ were calculated by the NB-MMMO-ELG- L_{\min} method at the level of ROHF/STO-3G for models 1 and 2. The starting cluster has 2 units, and 1 unit was added in each elongation step. Models 1 and 2 are huge systems for which large basis sets are hard to be used; moreover, it is more important to obtain correct order of values of L_{\min} and $\Delta E(L-H)$, thus, the basis set STO-3G was used as a first attempt. According to Table 1, values of $\Delta E(L-H)$ per unit for models 1 and 2 are about 0.351 a.u. and 0.347 a.u., respectively. As models 1 and 2 are periodic systems, $\Delta E(L-H)$ per unit should be constant. Therefore, the NB-MMMO-ELG- L_{\min} method can calculate $\Delta E(L-H)$ correctly. Table 1 shows that $\Delta E(L-H)$ increases with L_{\min} for models 1 and 2, respectively. In Table 1, for each number of unit, $\Delta E(L-H)$ of model 1 is larger than that of model 2, while L_{\min} of model 1 is also larger than that of model 2. That is, the greater the L_{\min} , the larger the $\Delta E(L-H)$. Table 1 shows that the value of $\Delta E(L-H)$ of model 2 for each number of unit is smaller than that of model 1. As the length of bond of Si-C is larger than that of C-C, the degree of delocalization of unpaired electron from the silicon atom to the ferromagnetic coupling unit is smaller than that from the carbon atom, which results in smaller exchange interaction between unpaired electrons and $\Delta E(L-H)$. The polarizable continuum model (PCM) is a popular method for treating solvent effects [4]. In Figure 3, L_{\min} and $\Delta E(L-H)$ were calculated by the NB-MMMO-ELG- L_{\min} method with PCM at the level of ROHF/STO-3G for model 2. Figure 3 shows that $\Delta E(L-H)$ also increases with L_{\min} under solvent effects.

In conclusion, the NB-MMMO-ELG- L_{\min} method is a promising method for predicting high spin stability in huge open-shell polymer systems and designing organic ferromagnets.

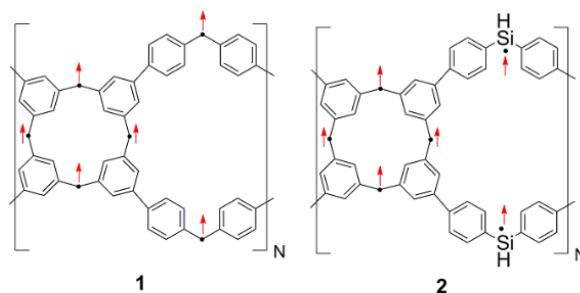


Figure 2 Selected models 1 and 2. Black dots are unpaired electrons, red arrows mean up spins.

Table 1 L_{\min} and $\Delta E(L-H)$ for model 1 (M1) and model 2 (M2).

unit	$\Delta E(L-H)/\text{a.u.}$		L_{\min}	
	M1	M2	M1	M2
2	0.709	0.697	0.070	0.069
3	1.060	1.044	0.106	0.105
4	1.411	1.391	0.142	0.140
5	1.762	1.739	0.178	0.175
6	2.113	2.086	0.214	0.210

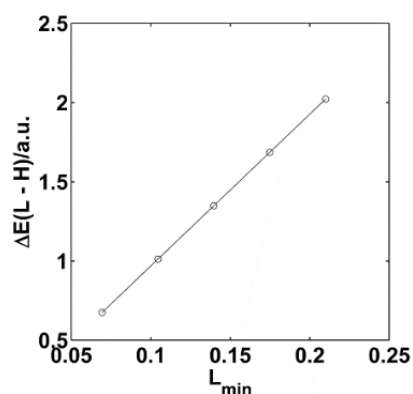


Figure 3 Relationship between L_{\min} and $\Delta E(L-H)$ with PCM for model 2.

References

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