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Open-shell ELG 法の開発と新規磁性材料設計への応用

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Development of open-shell elongation method and its application to ferromagnetic material design

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1. Introduction

Conventional (CONV) ab initio method has problem in treating huge systems as big time scale. Many linear scaling schemes including elongation (ELG) method[1] have been proposed during the last decades. Most linear scaling methods are still limited to closed-shell systems. It is very desired to extend the initial closed-shell ELG method to be able to treat open-shell systems such as organic molecule-based ferromagnets, which have many advantages and applications.[2, 3] We investigated the accuracy and efficiency of the developed open-shell elongation method for high-spin nonbonding butadiene radicals at the level of restricted open-shell Hartree-Fock (ROHF). Furthermore, we investigated the organic ferromagnetism using high-spin stability index L_{ij}^{min} based on the nonbonding molecular orbitals (NBMOs) obtained by ELG at the level of ROHF.

2. Method

2.1. Open-shell elongation method

A target system is divided into N units and each unit is assumed to have an unpaired electron with up spin (see Fig. 1). The eigenvalue problem of a starting cluster consisting of A and B parts is solved to initiate the elongation method. Canonical MOs of the starting cluster is localized into A_1 part and B part. Next, an attacking monomer M is added, and the eigenvalue problem of B and M is solved. After that, the B+M part is localized into A_2 part and B part. The procedure is repeated until the desired system size is reached. Cutoff technique can be included to speed up the calculations. As the eigenvalue problem is only solved for the B+M part, if the coupling between A_1 and B + M part is below threshold, A_1 part can be ignored during the self-consistent-field process without introducing big error in the next step. Finally, the total energy is calculated including the cutoff part.

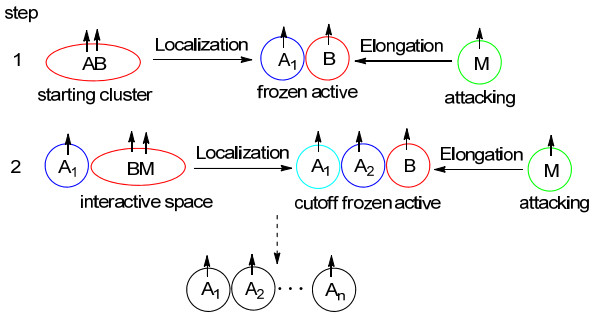


Figure 1. Flowchart of open-shell elongation method

2.2. High-spin stability index L_{ij}^{min}

As it is still a challenging problem to obtain the exact energy difference between the lowest spin state and the highest spin state for a system with degenerate NBMOs, a high-spin stability index L_{ij}^{min} was proposed for quick design of organic ferromagnets.[4] Based on the

NBMOs obtained by ELG method at the level of ROHF, we can obtain L_{ij}^{min} as following:

(1) Perform unitary transformation on NBMOs in iterative way as

$$\begin{pmatrix} \psi_i' \\ \psi_j' \end{pmatrix} = \begin{pmatrix} sin\theta & cos\theta \\ -cos\theta & sin\theta \end{pmatrix} \begin{pmatrix} \psi_i \\ \psi_j \end{pmatrix}, \quad (1)$$

where $\boldsymbol{\theta}$ is the transformation parameter and the optimized $\boldsymbol{\theta}$ generates the L_{ij}^{min} value that is the minimum overlap of coefficients of NBMOs. As L_{ij}^{min} varies with $\boldsymbol{\theta}$, $\boldsymbol{\theta}$ should be optimized in iterative way, and the detailed process of obtaining $\boldsymbol{\theta}$ can be seen in Ref. 4.

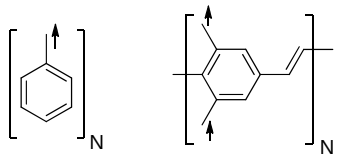
(2) Calculate the L_{ij}^{min} value[4, 5] as

$$L_{ij}^{min} = \sum_{j>i} \sum_{r} (C_{ir}' C_{jr}')^2, \quad (2)$$

where L_{ij}^{min} corresponds to the minimum energy difference between the lowest spin (L) state and the highest spin (H) state, that is, ΔE(L-H) = E(L) – E(H).

3. Results and discussion

We have performed calculations for model **1** in Fig. 2 at the ROHF/6-31G level of theory. The distance between two units is 6 Å for the test. The number of units in the starting cluster is 10, and 5 units are added each time. The first cutoff calculation started from 25 units. The threshold of density matrix is 10^{-8}. The deviation of energy (per atom) from the conventional calculation is shown in Fig. 3a. The largest deviation is 1.90×10^{-8} a.u. per atom. As shown in Fig. 3b, the CPU time of elongation method is faster than that of conventional method when the system is big enough. We have also performed ELG calculations at the level of ROHF/6-31G(d) for model **2** in Fig. 2 to obtain L_{ij}^{min}, the number of units in the starting cluster is 6, and 1 unit is added each time. ΔE(L-H) obtained by conventional method at the ROHF/6-31G(d) level can indicate the level of ferromagnetism. As shown in Fig. 4, ΔE(L-H) increases with L_{ij}^{min}, which means L_{ij}^{min} can indicate the degree of high-spin stability.



1 **2**

Figure 2. Selected models. Black arrows are unpaired electrons with up spin

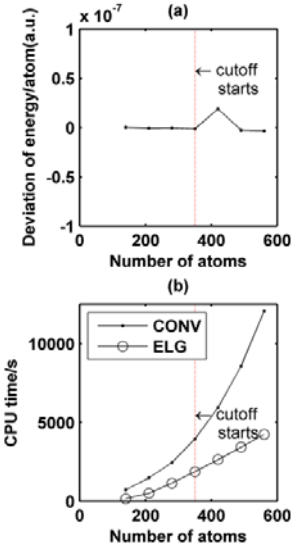


Figure 3. Comparison of energy and CPU time between ELG and conventional methods at the level of ROHF/6-31G for model **1**

It indicates that the combination between open-shell elongation method and L_{ij}^{min} index is promising for huge systems and quick design of organic ferromagnet.

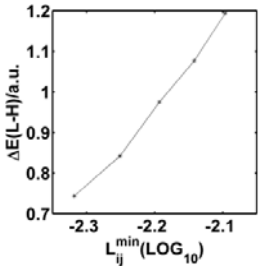


Figure 4. Variation of ΔE(L-H) with L_{ij}^{min} for model **2**

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