Efficient prediction of high spin ground state stability
in organic polyradicals under solvent effects

Xun Zhu^a, and Yuriko Aoki^{b,c}

^aDepartment of Molecular and Material Sciences, Interdisciplinary Graduate School of
Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816-8580, Japan

^bDepartment of Energy and Material Sciences, Faculty of Engineering Sciences,
Kyushu University, Kasuga, Fukuoka 816-8580, Japan

^cJapan Science and Technology Agency, CREST, 4-1-8 Hon-chou,
Kawaguchi, Saitama 332-0012, Japan

Corresponding author: Yuriko Aoki
E-mail: aoki.yuriko.397@m.kyushu-u.ac.jp
Tel/Fax: +81-92-583-8834

Abstract: When designing organic ferromagnets in nano- and bio-systems, it is essential to account for solvent effects as most biological reactions occur in water. The minimized mixing elongation (MMELG) method was combined with the polarizable continuum model (PCM) for accurate and efficient electronic structure calculations of the lowest and highest spin states of huge systems with solvent effects. The MMELG-PCM- $L_{\min}$ method that combined the MMELG-PCM method and the $L_{\min}$ method can be efficiently and reliably applied to predict the high spin ground state stability of conjugated organic polyradicals and is thus useful for designing organic ferromagnets with solvent effects.

Keywords: high spin ground state stability, minimized mixing elongation method, organic ferromagnets, polarizable continuum model, solvent effects

1. Introduction

Organic ferromagnets are attracting increased attention due to their unique properties, such as their solubility in organic solvents, and potential applications in fields such as spintronics [1-3]. Conjugated organic polyradicals that have strong exchange interaction between spin-containing units have been studied theoretically and experimentally [4, 5]. In 2001, Rajca et al. synthesized conjugated organic polyradicals with spin quantum numbers (S) greater than 5000 [6].

To utilize organic ferromagnets in bio-systems, it is necessary to account for solvent effects. Many methods such as the polarizable continuum model (PCM) have been developed to model solvent effects [7-9]. The elongation method has been developed and proven to be accurate and efficient for large systems [10-13]. In 2012, the elongation-PCM method that combined the elongation method and the PCM was developed for large neutral biopolymers [14, 15].

In 2015, we developed the minimized mixing elongation (MMELG) method and the $L_{\min}$ method at the ab initio level for predicting the high spin ground state stability of conjugated organic radicals [16]. This is reflected by $\Delta E(L - H)$, which is the difference between the energy of the lowest spin state [$E(L)$] and that of the highest spin state [$E(H)$] [where $\Delta E(L - H) = E(L) - E(H)$]. The MMELG method uses the minimized mixing molecular orbital (MMMO) method to localize the singly occupied molecular orbitals and the regional localized molecular orbital (RLMO) method to localize the doubly occupied and vacant molecular orbitals [11, 16]. In order to predict $\Delta E(L - H)$ of conjugated organic radicals, a method with an index $L_{\min}$ called $L_{\min}$ method was developed [16]. In this method, the index $L_{\min}$ defined as minimized mixing between coefficients of nonbonding molecular orbitals (NBMOs) reflects the high spin ground state stability of conjugated organic radicals. As the NBMOs are degenerate, in order to determine the unique

exchange integral between NBMOs corresponding to the high spin ground state stability, the coefficients of NBMOs should be localized to find the minimum value of $L_{\min}$.

In this study, we developed the MMELG-PCM method that combines the MMELG method and the PCM for high spin open-shell systems with solvent effects. In each elongation step, the term corresponding to the PCM was added to α and β Fock matrices, after which the Fock matrix of the whole system for the ROHF calculation was constructed and reduced to the size of the active part for which the eigenvalue problem was solved. That is, the PCM is treated for the active part other than the whole system during the self-consistent field (SCF) calculation in each elongation step. We called MMELG-PCM method for this way of treatment of PCM by the MMELG method. The MMELG-PCM method can be combined with the $L_{\min}$ method to predict $\Delta E(L - H)$ of conjugated organic radicals with solvent effects and is thus useful for designing organic ferromagnets for applications in bio-systems.

2. Method

Suppose a system in a solvent is constructed with many units and each unit has an unpaired electron with up spin (Figure 1). In the first step, the canonical molecular orbitals (CMOs) of the starting cluster ($A + B$) are calculated by the conventional (CONV) method to trigger the calculation. Some of the CMOs are then localized on the A part and the others are localized on the B part. In the next elongation step, the A part is defined as the frozen part and the B part is defined as the active part. In this study, the doubly occupied and vacant molecular orbitals were localized by the RLMO localization method and the singly occupied molecular orbitals were localized by the MMMO localization method [11, 16]. In the second step, a monomer C was added to the B part and the CMOs of the $B + C$ part were calculated by the MMELG method, after which the

CMOs of $B + C$ were localized by the RLMO and MIMO localization methods. This procedure was repeated until the entire system was calculated.

The MMELG-PCM method, formulated by the combination of the MMELG method and the PCM, was combined with the GAMESS program package [17]. A description of the first elongation step is provided to show the procedure of the MMELG-PCM method. In the first elongation step, the A part was the frozen part and the $B + M$ part was the active part. A term describing solvent effects was added to the Fock matrix as follows:

$$V_{\mu\nu} = \left\langle \mu \left| \int \frac{\sigma(s)}{|r-s|} d^2s \right| \nu \right\rangle, \quad (1)$$

where $V_{\mu\nu}$ is the matrix element of electrostatic potential and $\sigma(s)$ is the surface charge distribution. In the MMELG-PCM method, the Fock matrices for α and β spins can be described as follows:

$$F_{\mu\nu}^{\alpha(PCM)} = F_{\mu\nu}^{\alpha}(A|B+M) + V_{\mu\nu}, \quad (2)$$

$$F_{\mu\nu}^{\beta(PCM)} = F_{\mu\nu}^{\beta}(A|B+M) + V_{\mu\nu}, \quad (3)$$

where $F_{\mu\nu}^{\alpha}(A|B+M)$ is the matrix element of a solute Fock matrix with α spin and $F_{\mu\nu}^{\beta}(A|B+M)$ is the matrix element of a solute Fock matrix with β spin. In $F_{\mu\nu}^{\alpha}(A|B+M)$ and $F_{\mu\nu}^{\beta}(A|B+M)$, $(A|B+M)$ represents the whole system, where the A part is the frozen part that will increase in size as the size of the system increases and the $B + M$ part is the active part. Eqs. (2) and (3) were used to construct the Fock matrix $\mathbf{F}(A|B+M)$, which was transformed to $\mathbf{F}_{(B+M)}^{\text{MO}}$ of the active part. The eigenvalue problem was solved for the active part as follows:

$$\mathbf{F}_{(B+M)}^{\text{MO}} \mathbf{C}_{(B+M)}^{\text{MO}} = \mathbf{S}_{(B+M)}^{\text{MO}} \mathbf{C}_{(B+M)}^{\text{MO}} \boldsymbol{\epsilon}_{(B+M)}, \quad (4)$$

where $\mathbf{C}_{(B+M)}^{\text{MO}}$ is the coefficient matrix, $\mathbf{S}_{(B+M)}^{\text{MO}}$ is the overlap matrix, and $\boldsymbol{\epsilon}_{(B+M)}$ is the eigenvalue matrix. In Eq. (4), $\mathbf{S}_{(B+M)}^{\text{MO}}$ was diagonalized once to obtain the transformation matrix during the SCF calculation. Eq. (4) was then transformed as follows:

$$\mathbf{F}_{(B+M)}^{\text{MO}} \mathbf{C}_{(B+M)}^{\text{MO}} = \mathbf{C}_{(B+M)}^{\text{MO}} \boldsymbol{\epsilon}_{(B+M)}. \quad (5)$$

After solving Eq. (5), $\mathbf{C}_{(B+M)}^{\text{MO}}$ was transformed back to $\mathbf{C}_{(B+M)}^{\text{MO}}$, which was then transformed to $\mathbf{C}_{(B+M)}^{\text{AO}}$. In each molecular orbital of $\mathbf{C}_{(B+M)}^{\text{AO}}$, the coefficients were mainly derived from the $B + M$ part. After this process, the coefficient matrices of the whole system were constructed, new density matrices of the whole system were calculated and compared with the old ones, and the cycle was repeated until the criterion of convergence was reached.

The coefficients of NBMOs generated by the MMELG-PCM method were then used to calculate the value of $L_{\min}$ by the $L_{\min}$ method for predicting $\Delta E(\text{L} - \text{H})$ of conjugated organic radicals. The $L_{\min}$ method is briefly described as follows. The relationship between $\Delta E(S - T)$ and $L_{\min}$ was derived as:

$$\begin{aligned} \Delta E(S - T) &= 2K_{ij} = 2 \sum_{rstu} C_{ri} C_{sj} C_{ti} C_{uj} (rs | tu) \\ &\approx 2 \sum_r \left(C_{ri} C_{rj} \right)^2 (rr | rr) = 2L_{ij}^{\min} (rr | rr), \end{aligned} \quad (6)$$

where r, s, t , and u refer to atomic orbitals (AOs); i and j refer to the i th NBMO (NBMO $_i$) and j th NBMO (NBMO $_j$), respectively; $\Delta E(S - T)$ is the energy difference between singlet and triplet states; K_{ij} is the exchange integral between NBMO $_i$ and NBMO $_j$; and C_{ri} is the coefficient of NBMO $_i$. Assuming that $(rr | rr)$ was constant, then

$$\Delta E(S - T) \propto L_{\min}. \quad (7)$$

The relationship between K and $L_{\min}$ was derived as follows:

$$K = \sum_{j>i} K_{ij} \approx \sum_{j>i} L_{ij}^{\min} (rr | rr) = L_{\min} (rr | rr). \quad (8)$$

The value of $L_{\min}$ was calculated using the localized coefficients of NBMOs as follows:

$$L_{\min} = \sum_{j>i} L_{ij}^{\min} = \sum_{j>i} \sum_r (C_{ri} C_{rj})^2, \quad (9)$$

where r refers to the r th AO; i and j refer to NBMO $_i$ and NBMO $_j$, respectively; and C_{ri} and C_{rj} are the coefficients of NBMO $_i$ and NBMO $_j$, respectively.

3. Results and Discussion

Model **1** in Figure 2 was the same as polymer **1** in Ref. 6 with the exception that the tert-butylbenzene group was replaced by hydrogen. As model **1** is periodic system, one part of model **1** was optimized at the level of UB3LYP/6-31G(d) by the Gaussian 09 program package [18], when was then used as a repeated unit to construct the whole system for the subsequent calculations of $L_{\min}$ and $\Delta E(L - H)$ performed in the GAMESS program package [17].

The values of $\Delta E(L - H)/\text{ELG}$ and $\Delta E(L - H)/\text{CONV}$ were calculated by the MMELG-PCM method and CONV method at the level of ROHF/6-31G, respectively (Figure 3a). The total spin quantum numbers of the highest spin states were 6, ..., 21 and those of the lowest spin states were 0 when $N = 2, \dots, 7$ as shown in Table 1. Here water was used as solvent to test the MMELG-PCM method. The values of $\Delta E(L - H)$ of model **1** in Figure 3a calculated at the level of ROHF that did not consider the correlation effects appeared to be large; however, these values show the correct order of the values of $\Delta E(L - H)$ of different N . For model **1** with different N when the correlation effects are considered, the order of the values of $\Delta E(L - H)$ will not change (See Figure 4c in Ref. 19). Figure 3a shows that both $\Delta E(L - H)/\text{ELG}$ and $\Delta E(L - H)/\text{CONV}$

increased with the number of units (N). As shown in Figure 3a, $\Delta E(L - H)/ELG$ increased with N linearly, whereas $\Delta E(L - H)/CONV$ did not increase with N linearly. In Figure 3b, $\Delta E(N)$ means $\Delta E(L - H)$ with N units, $\Delta E(N - 1)$ means $\Delta E(L - H)$ with $N - 1$ units, $[\Delta E(N) - \Delta E(N - 1)]$ means $\Delta E(N) - \Delta E(N - 1)$, $[\Delta E(N) - \Delta E(N - 1)]/ELG$ means $[\Delta E(N) - \Delta E(N - 1)]$ for the MMELG-PCM method, and $[\Delta E(N) - \Delta E(N - 1)]/CONV$ means $[\Delta E(N) - \Delta E(N - 1)]$ for the CONV method. The values of $[\Delta E(N) - \Delta E(N - 1)]$ in Figure 3b seem to be large, they can prove the validity of the MMELG-PCM method for calculating $\Delta E(L - H)$ and can be reduced when correlation effects are considered. As model 1 was a periodic system, $\Delta E(N) - \Delta E(N - 1)$ should be constant. Figure 3b shows that $[\Delta E(N) - \Delta E(N - 1)]/ELG$ was almost constant. In contrast, $[\Delta E(N) - \Delta E(N - 1)]/CONV$ sharply deviated from the average value of $[\Delta E(N) - \Delta E(N - 1)]/CONV$ at three points. As the lowest spin state is an open-shell singlet in which half of all the unpaired electrons have up spin and half of the others have down spin, it is difficult for a single-reference method to model. In one CMO, two unpaired electrons come from two atoms; thus, the coefficients should be focused on the two atoms. However, the CMOs are delocalized in the CONV method. As half of the unpaired electrons have up spin and half have down spin, the total energy of the lowest spin state calculated by the CONV method may be lower than the correct value. In contrast, the coefficients of each CMO in the MMELG method are localized on the two atoms containing the two unpaired electrons in each elongation step. In the conventional calculation, increasing numbers of unpaired electrons are involved as the size of the system increases, and this causes an increase in the order of complexity of the SCF calculation. As the MMELG method assumes that the system has a constant size during the SCF calculation, the number of unpaired electrons involved in the calculation is constant, which reduces the order of complexity. The lowest spin state of open-shell systems has a multi-reference nature as there are many electronic configurations. Suppose that

each NBMO is occupied by one unpaired electron, the number of electronic configurations (N_{ec}) of the low spin states of an open-shell system is as follows:

$$N_{ec} = 2^n - 2, \quad (10)$$

where n is the number of unpaired electrons. As n increases, the value of N_{ec} will increase at a rapid rate (e.g., when $n = 2$, $N_{ec} = 2$ [20]; when $n = 12$, $N_{ec} = 4094$; and when $n = 42$, $N_{ec} \approx 4.4 \times 10^{12}$). Because the MMELG assumes that the open-shell system has a constant size during the SCF calculation, N_{ec} will also be constant, making the MMELG method more accurate compared with the CONV method when treating the lowest spin state of open-shell systems.

The values of $L_{\min}(\text{ELG})$ and $L_{\min}(\text{CONV})$ of model **1** were calculated by the MMELG-PCM- $L_{\min}$ method and CONV method at the level of ROHF/6-31G (Figure 4). Because $L_{\min}(\text{ELG})$ was the same as $L_{\min}(\text{CONV})$, as shown in Figure 4, the MMELG-PCM- $L_{\min}$ method could produce correct values of $L_{\min}$ for model **1**.

Figure 5a shows the calculations of $\Delta E(\text{L} - \text{H})$ and $L_{\min}$ of model **1** by the MMELG-PCM- $L_{\min}$ method at the level of ROHF/6-31G. The results showed that $\Delta E(\text{L} - \text{H})$ increased with $L_{\min}$. Figure 5b shows the calculations of $\Delta E(\text{L} - \text{H})$ and $L_{\min}$ of model **1** by the MMELG- $L_{\min}$ method at the level of ROHF/6-31G, where the results showed that $\Delta E(\text{L} - \text{H})$ also increased with $L_{\min}$. Therefore, $\Delta E(\text{L} - \text{H})$ of conjugated organic radicals such as model **1** in a solvent could be reliably predicted by $L_{\min}$ calculated by the MMELG-PCM- $L_{\min}$ and the MMELG- $L_{\min}$ methods.

Spin density distributions were also calculated for model **1** with different N at the level of UHF/6-31G by the Gaussian 09 program package [18]. Figure 6 shows that positive and negative spin densities of model **1** with different N appeared alternately, indicating that they are the highest spin state for different N . Furthermore, as shown in Figure 6, the spin density in the ferromagnetic

coupling unit is large, indicating that there are strong spin polarization effects and exchange interaction between unpaired electrons, which leads to large $\Delta E(L - H)$ (see Figure 7 in Ref. 5).

4. Conclusions

The MMELG-PCM method was developed. The results showed that the MMELG-PCM method can treat the lowest spin state of huge open-shell systems, which are difficult or impossible to be treated correctly when using conventional methods. The MMELG-PCM method can also be combined with the $L_{\min}$ method to predict $\Delta E(L - H)$ of conjugated organic radicals with solvent effects and is thus useful for designing organic ferromagnets.

Acknowledgments

This work was supported by a grant-in-aid from the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT), Grant-in-Aid for Scientific Research(A) No. 23245005 and by the Group CREST, Japan Science and Technology Agency (JST). The calculations were performed on the Linux cluster in our laboratory at Kyushu University.

References

- [1] X. Zhu, Y. Aoki, Curr. Phys. Chem. 3 (2013) 99.
- [2] J.S. Miller, Mater. Today 17 (2014) 224.
- [3] V. Barone, C. Boilleau, I. Cacelli, A. Ferretti, S. Monti, G. Prampolini, J. Chem. Theory Comput. 9 (2013) 300.
- [4] Y. Orimoto, Y. Aoki, J. Chem. Theory Comput. 2 (2006) 786.
- [5] N.M. Gallagher, A. Olankitwanit, A. Rajca, J. Org. Chem. 80 (2015) 1291.

- [6] A. Rajca, J. Wongsriratanakul, S. Rajca, *Science* 294 (2001) 1503.
- [7] J. Tomasi, M. Persico, *Chem. Rev.* 94 (1994) 2027.
- [8] M. Cossi, V. Barone, R. Cammi, J. Tomasi, *Chem. Phys. Lett.* 255 (1996) 327.
- [9] J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.* 105 (2005) 2999.
- [10] A. Imamura, Y. Aoki, K. Maekawa, *J. Chem. Phys.* 95 (1991) 5419.
- [11] F.L. Gu, Y. Aoki, J. Korchowiec, A. Imamura, B. Kirtman, *J. Chem. Phys.* 121 (2004) 10385.
- [12] J. Korchowiec, F.L. Gu, Y. Aoki, *Int. J. Quantum. Chem.* 105 (2005) 875.
- [13] Y. Orimoto, R. Yamamoto, P. Xie, K. Liu, A. Imamura, Y. Aoki, *J. Chem. Phys.* 142 (2015) 104111.
- [14] Y. Aoki, F.L. Gu, Y. Orimoto, S. Suhai, A. Imamura, *AIP Conf. Proc.* 963 (2007) 120.
- [15] Y. Aoki, F.L. Gu, *Phys. Chem. Chem. Phys.* 14 (2012) 7640.
- [16] X. Zhu, Y. Aoki, *J. Comput. Chem.* 36 (2015) 1232.
- [17] M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S. Su, T.L. Windus, M. Dupuis, J.A. Montgomery, *J. Comput. Chem.* 14 (1993) 1347.
- [18] Gaussian 09, Revision C.01, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A.J. Montgomery, J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev,

A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J. V. Ortiz, J. Cioslowski, D.J. Fox. (2010) Gaussian, Inc., Wallingford CT.

[19] Y. Orimoto, T. Imai, K. Naka, Y. Aoki, J. Phys. Chem. A 110 (2006) 5803.

[20] M. Abe, Chem. Rev. 113 (2013) 7011.

Figure Captions

Figure 1 Schematic illustration of the MMELG-PCM method

Figure 2 Model **1** selected. Dots are unpaired electrons, red arrows near the unpaired electrons mean up spins.

Figure 3 (a) $\Delta E(L - H)$ and (b) $\Delta E(L - H)$ per unit calculated by the MMELG-PCM and CONV methods at the level of ROHF/6-31G for model **1**.

Figure 4 $L_{\min}$ calculated by the MMELG-PCM- $L_{\min}$ and CONV methods at the level of ROHF/6-31G for model **1**.

Figure 5 (a) Relationship between $L_{\min}$ and $\Delta E(L - H)$ calculated by the MMELG-PCM- $L_{\min}$ method at the level of ROHF/6-31G for model **1**. (b) Relationship between $L_{\min}$ and $\Delta E(L - H)$ calculated by the MMELG- $L_{\min}$ method at the level of ROHF/6-31G for model **1**.

Figure 6 Spin density distributions calculated at the level of UHF/6-31G for model **1** with different N (Isovalue = 0.0004, blue for positive spin density, green for negative spin density).

Table 1

Table 1 Values of S/H and S/L for model **1** with different N , N is the number of units, N_{se} is the number of unpaired electrons, S is the total spin quantum number, H is the highest spin state, L is the lowest spin state.

N	N_{se}	S/H	S/L
2	12	6	0
3	18	9	0
4	24	12	0
5	30	15	0
6	36	18	0
7	42	21	0

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

$N = 2$

$N = 3$

$N = 4$

$N = 5$

$N = 6$

$N = 7$