New Reaction Simulator “LUMMOX” and Its Application for Prediction of Catalytic Activities

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Abstract: We developed a new reaction simulator, “LUMMOX.” It is an intermolecular interaction analyzer based on the theories of paired interacting orbitals (PIOs) and localized frontier orbitals (LFOs) that have been developed by Fujimoto et al. (Fukui, K.; Koga, N.; Fujimoto, H. J Am Chem Soc 1981, 103, 196; Fujimoto, H.; Koga, N.; Fukui, K. J Am Chem Soc 1981, 103, 7452; Fujimoto, H.; Satoh, S. J Phys Chem 1994, 98, 1436). LUMMOX runs on a Windows PC and displays graphic representation of orbital interactions. Prediction of activities, selectivities, and molecular weight of olefin polymerization catalysts are presented using PIO analysis and LFO calculation. Not only computational chemists but also experimental chemists can easily use this new system for catalyst design or molecular design from the point of view of orbital interaction.


Key words: paired interacting orbitals; localized frontier orbitals; reaction path; olefin polymerization; catalysis

Introduction

“LUMMOX” is a new reaction simulator that consists of four subsystems:

1. Canonical molecular orbital calculation and paired interacting orbital (PIO) calculation subsystem.
2. Graphical displays of paired interacting orbitals and canonical molecular orbitals.
3. Localized frontier orbital (LFO) calculation subsystem.
4. Coordinate transformation from Z-matrix to Cartesian coordinate.

As for the first subsystem, the canonical molecular orbital (MO) calculation is done using the extended Hückel method based on the Wolfsberg–Helmholtz method. LUMMOX is built using Visual Basic 6.0 and Visual C++ 6.0 and runs on Windows 95. LUMMOX means Least Unified Meta-Molecular Orbital Calculation System.

We present here the algorithms of PIO and LFO calculations and show some examples of applying LUMMOX for prediction of catalytic activities.

Algorithm of Paired Interacting Orbitals

When we investigate the interaction between two molecules A and B, we call the interacting system C.

The molecular orbitals \( \{ \varphi_i \} \) \((i = 1, \ldots, s)\) of A are expanded using the atomic orbitals \( \{ \chi_{A,i} \} \) \((i = 1, \ldots, s)\) of A. The MOs \( \{ \psi_j \} \) \((j = 1, \ldots, t)\) of B are also expanded using the atomic orbitals \( \{ \chi_{B,j} \} \) \((j = 1, \ldots, t)\) of B:

\[
\varphi_i = \sum_{k=1}^{s} A_{i,k} \chi_{A,k} \quad (i = 1, \ldots, s) \quad (1)
\]

\[
\psi_j = \sum_{k=1}^{t} B_{j,k} \chi_{B,k} \quad (j = 1, \ldots, t) \quad (s \leq t). \quad (2)
\]

The MOs \( \{ \Phi_k \} \) \((k = 1, \ldots, s + t)\) of the interacting system C can be expanded using the atomic orbitals \( \{ \chi_{A,i} \} \) of A and the atomic orbitals \( \{ \chi_{B,j} \} \) of B. Here, the MOs \( \{ \Phi_k \} \) of C can also be expanded using the MOs \( \{ \varphi_i \} \) of A and \( \{ \psi_j \} \) of B:

\[
\Phi_k = \sum_{i=1}^{s} C_{i,k} \varphi_i + \sum_{j=1}^{t} D_{j,k} \psi_j \quad (k = 1, \ldots, s + t) \quad (3)
\]

\[
= \sum_{i=1}^{s} C_{i,k} \varphi_i + \sum_{j=1}^{t} D_{j,k} \psi_j \quad (k = 1, \ldots, s + t). \quad (4)
\]
Using these $C_{i,k}$ and $D_{j,k}$, we define the interaction matrix:

$$P_0 = \sum_{k=1}^{s+t} v_k C_{i,k} D_{j,k} \quad (i = 1, \ldots, s, \quad j = 1, \ldots, t). \quad (5)$$

Here, $v_k$ means the number of electrons in orbital $k$.

This matrix $P$ is a rectangular matrix in general, and the diagonalization of $P$ is a general eigenvalue problem. The problem is that we have to find the unitary matrixes $V$ and $U$ to obtain the diagonal matrix $T$:

$$V^T P U = T. \quad (6)$$

Multiplying $P$ by $P^T$ from the left side, matrix $P^TP$ is obtained. The matrix element $Q_{ij}$ is

$$Q_{ij} = \sum_{k=1}^{s+t} P_{ik} P_{kj} \quad (i = 1, \ldots, t \quad j = 1, \ldots, t). \quad (7)$$

Thus, this matrix $(Q_{ij})$ is Hermitian and can be diagonalized by unitary transformation shown in formula (8):

$$P^T P U = U \Lambda. \quad (8)$$

This formula can be rewritten in the following formula:

$$(PU)^T(PU) = \Lambda. \quad (9)$$

Therefore, $PU$ can be written in formulate (10), where $V$ is unitary:

$$PU = VT. \quad (10)$$

Thus, the diagonal matrix $T$ is obtained:

$$T = \Lambda^{1/2}. \quad (11)$$

Therefore, the unitary matrix $V$ is obtained from (10) and (11):

$$V = PU \Lambda^{-1/2}. \quad (12)$$

Here, the diagonal element of $\Lambda$, which is $\lambda_i$ $(i = 1, \ldots, s)$, means the square of interaction strength. Making unitary transformation of $\varphi_i$, $\psi_i$ using $V$ and $U$, the transformed orbitals $\varphi^*_i$, $\psi^*_i$ can be obtained as shown in formulate (13) and (14) where paired orbitals $\{\varphi^*_i, \psi^*_i\}$ $(i = 1, \ldots, s)$ are interacting:

$$\varphi^*_i = \lambda_i^{1/2} \sum_{j=1}^{s} \sum_{k=1}^{t} P_{j,k} U_{j,k} \phi_j \quad (i = 1, \ldots, s) \quad (13)$$

$$\psi^*_i = \sum_{j=1}^{t} U_{j,i} \phi_j \quad (i = 1, \ldots, t). \quad (14)$$

Thus, the MOs $\{\Phi_k\}$ are reformulated using $\{\varphi^*_i\}$ and $\{\psi^*_i\}$:

$$\Phi_k = \sum_{i=1}^{s+t} C_{i,k} \varphi^*_i + \sum_{j=1}^{s+t} D_{j,k} \psi^*_j \quad (k = 1, \ldots, s + t). \quad (15)$$

Therefore, MO population and MO bond population (overlap population) are formulated:

$$N_i = \sum_{k=1}^{s+t} v_k C^*_{i,k} C_{i,k} \quad \text{for } \varphi^*_i \quad (i = 1, \ldots, s) \quad (16)$$

$$N_j = \sum_{k=1}^{s+t} v_k D^*_{j,k} D_{j,k} \quad \text{for } \psi^*_j \quad (j = 1, \ldots, t) \quad (17)$$

$$N_{ij} = 2 \sum_{k=1}^{s+t} v_k C^*_{i,k} D^*_{j,k} \langle \varphi^*_i | \psi^*_j \rangle \quad (i = 1, \ldots, s). \quad (18)$$

**Algorithm of LFOs**

Reference orbital $\delta_r$, represented using an atomic orbital or a linear combination of atomic orbitals within a molecule, can be expanded using molecular orbitals $\{\phi_i\}$ of the molecule:

$$\delta_r = \sum_{i=1}^{\text{occ}} D_{i,r} \phi_i + \sum_{i=\text{unocc}+1}^{\text{occ}} D_{i,r} \phi_i \quad \text{ (19)}$$

Usually reference orbital $\delta_r$ is a reaction-related orbital.

We define occupied LFO $\psi_{\text{occ}}(\delta_r)$ as shown in (20), where $\psi_{\text{occ}}(\delta_r)$ is expanded using the above occupied MOs and normalized. And, we also define unoccupied LFO $\psi_{\text{unocc}}(\delta_r)$ as shown in (21), where $\psi_{\text{unocc}}(\delta_r)$ is expanded using the above unoccupied MOs and normalized:

$$\psi_{\text{occ}}(\delta_r) = \sum_{i=1}^{\text{occ}} D_{i,r} \phi_i \left( \sum_{i=1}^{\text{occ}} D^*_{i,r} \right)^{1/2} \quad (20)$$

$$\psi_{\text{unocc}}(\delta_r) = \sum_{i=\text{unocc}+1}^{\text{occ}} D_{i,r} \phi_i \left( \sum_{i=\text{occ}+1}^{\text{unocc}} D^*_{i,r} \right)^{1/2}. \quad (21)$$

The expected values of the LFOs are

$$\lambda_{\text{occ}}(\delta_r) = \sum_{i=1}^{\text{occ}} D^*_{i,r} E_{i} \left( \sum_{i=1}^{\text{occ}} D_{i,r} \right) \quad (22)$$

$$\lambda_{\text{unocc}}(\delta_r) = \sum_{i=\text{occ}+1}^{\text{unocc}} D^*_{i,r} E_{i} \left( \sum_{i=\text{occ}+1}^{\text{unocc}} D_{i,r} \right). \quad (23)$$
Here, $e_i$ is an energy value of the MO $\psi_i$ of the molecule. From (19), (20), and (21), we can get

$$\delta_i = \left( \sum_{r=1}^{\text{occ}} D_{i,r}^2 \right)^{1/2} \psi_{\text{occ}}(\delta_i) + \left( \sum_{r=\text{unocc}+1}^{\text{unocc}} D_{i,r}^2 \right)^{1/2} \psi_{\text{unocc}}(\delta_i).$$

(24)

Here, we define $a^2$ as

$$a^2 = \sum_{i=1}^{\text{occ}} D_{i,r}^2.$$  

(25)

Therefore,

$$\delta_i = a \psi_{\text{occ}}(\delta_i) + (1 - a^2)^{1/2} \psi_{\text{unocc}}(\delta_i).$$  

(26)

The expected value of energy of $\delta_i$ is

$$\lambda(\delta_i) = \sum_{i=1}^{\text{occ}} D_{i,r}^2 \delta_i + \sum_{i=\text{unocc}+1}^{\text{unocc}} D_{i,r}^2 \delta_i.$$  

(27)

From (22), (23), and (27), (28) is obtained:

$$\lambda(\delta_i) = a^2 \lambda_{\text{occ}}(\delta_i) + (1 - a^2) \lambda_{\text{unocc}}(\delta_i).$$  

(28)

Here, local hardness $N(\delta_i)$ of reference orbital $\delta_i$ is defined:

$$N(\delta_i) = \frac{1}{2} \left( \lambda_{\text{unocc}}(\delta_i) - \lambda_{\text{occ}}(\delta_i) \right).$$  

(29)

Using $a^2$ and $N(\delta_i)$, we can calculate local acidic hardness $2a^2 N(\delta_i)$ and local basic hardness $2(1 - a^2) N(\delta_i)$.

**Examples of Applying LUMMOX for Prediction of Catalytic Activities**

**Prediction of Molecular Weight of Polypropylene Polymerized on Metallocene Catalysts Using PIO Analysis**

**Introduction**

Prediction of activities, selectivities, and molecular weight of polymers of polymerization catalysts is crucial for the development of polyolefin catalysts. Prediction based on the precise understanding of the reaction mechanism is indispensable. According to the approach of the catalyst and reactant along the reaction path, the deformation of the structure of them begins to take place. Instantaneously, electron delocalization from old bonds to reaction regions also begins to take place. The larger the amount of this delocalized electrons, the more favorably the reaction takes place. The reaction regions and the amount of delocalized electrons are determined by the PIO analysis. We use the total overlap population of all PIOs as an indicator of catalytic reactions. Here, propylene insertion and chain transfer to monomer on $[\text{iBuZrH}_2\text{SiCp}_2]^+$ (1), $[\text{iBuZrH}_2\text{Si(2-MeCp)Cp}]^+$ (2), $[\text{iBuZrH}_2\text{Si(3-MeCp)Cp}]^+$ (3), $[\text{iBuZrH}_2\text{Si(4-MeCp)Cp}]^+$ (4), $[\text{iBuZrH}_2\text{Si(5-MeCp)Cp}]^+$ (5), $[\text{iBuZrH}_2\text{Si(2-MeInd)}_2]^+$ (6), $[\text{iBuZrH}_2\text{Si(2-MeInd)}_2]^+$ (7), and $[\text{iBuZrH}_2\text{Si(3-MeInd)}_2]^+$ (8) are studied.
Models and Calculation Methods

A schematic illustration of silylene bridged zirconocene moiety is shown in Figure 1. We have examined the intermediate states of three main elementary reactions: (a) insertion, (b) chain transfer to monomer, and (c) β-H elimination of each models. The geometry optimization technique was not adopted for determining the structures of these states of the models. We assumed their structures referring the reported structures previously.\(^6\) They are shown in Figure 2.

All calculations, that is, MOs based on the extended Hückel method and PIOs applying the procedure proposed by Fujimoto, were carried out on LUMMOX.\(^7\)

Results and Discussion

Total overlap population (ΣOP) of PIOs of the intermediate state of olefin insertion, chain transfer to monomer, and β-H elimination on the silylene-bridged metallocene catalysts (1)–(8) are summarized in Table 1. We can estimate the reaction activities from the ΣOP values; the larger the ΣOP, the larger the insertion activities and the smaller the elimination.

Degree of polymerization is shown by

\[
\frac{1}{P_n} = \frac{k_{\text{insert}}}{k_p} + \frac{k_{\text{tr}}}{k_p} [M],
\]

where \(k_p\) is the rate constant of insertion, \(k_{\text{tr}}\) the rate constant of transfer to monomer, and \(k_{\text{insert}}\) the rate constant of β-H elimination.

Because the ΣOP of β-H elimination is markedly large in comparison with the ΣOP of insertion and transfer to monomer, it is reasonable to neglect the β-H elimination from the chain transfer reaction. Now, the degree of polymerization is simply expressed by \(k_p/k_{\text{tr}}\).

According to the ΣOP, we can estimate the order of insertion and transfer to monomer as follow: order of insertion

\(5 > 3 > 6 > 7 > 4 > 8\),

and order of transfer to monomer

\(2 > 1 > 5 > 3 > 6 > 8 > 4 > 7\).

As a result, the molecular weight of polypropylene has been predicted in the following order (highest to lowest): \(7 > 4 > 6 > 8 > 3 > 5 > 1 > 2\), and this result has shown good agreement with experimental results.\(^8\)

Index of Ethylene Insertion Activities on Methyltitanium Complexes Using LFO Calculation

Models

We employed ethylene insertion on \([\text{O}^{1\text{st}}_n\text{CH}_3\text{MCL}_4]^{-1}\) (M = Ti, Zr) and \([\text{T}^{1\text{st}}_n\text{CH}_3\text{ML}_2]^{10}\) (M = Ti, Zr; L = Cl, Cp). We analyzed an intermediate near transition state based on the Cossee insertion mechanism. The geometry optimization technique was not adopted for determining the structures of the states of the models. We assumed their structures referring to the reported structures previously.\(^9\) Schematic illustrations of the models are shown in Figures 3 and 4.

PIO Analysis and LFO Calculation

The most simple model of active site is \([\text{methyl-Ti}]^{3+}\). First, we obtained PIOs of the intermediate state of the \([\text{methyl-Ti}]^{3+}/\text{C}_2\text{H}_4\)
system. Here, the [methyl-Ti]$^+^3$ part is fragment [A] and the ethylene part is fragment [B]. The contour maps of PIO-1 and PIO-2 are shown in Figure 5.

The PIO-1 (the strongest interacting orbitals) represents the interaction between the lowest unoccupied MO (LUMO) of methyltitanium and the highest occupied MO (HOMO) of ethylene. It is mainly composed of $3dx^2$ and $3dz^2$ of titanium and $2pz$ of two ethylene carbons. The PIO-2 (the second strongest interacting orbitals) represents the interaction between the HOMO of methyltitanium and the LUMO of ethylene. It is mainly composed of $2px$, $2pz$ of methyl carbon, $3dx^2$ and $3dz$ of titanium, and $2ps$ of two carbons in ethylene.

Referring to PIO-1 and PIO-2, we determined reference orbitals for fragment [B]$^+^0$ paired with fragment [A]$^+_0$, and fragment [A]$^+^0$ paired with fragment [B]$^+_0$, as follows:

\[
(\delta_i)_{\text{base}} = -0.89^0C2p_x - 0.21^0C2px
\]
\[
(\delta_i)_{\text{LUMO}} = 0.28Ti4s + 0.44Ti3d_{z2} - 0.80Ti3d_{z2}
\]
\[
(\delta_i)_{\text{HOMO}} = -0.35Ti4s + 0.35Ti3d_{z2} - 0.32Ti3d_{z2}
-0.20C2px_Cp_s + 0.46C2p_x + 0.49C2p_z.
\]
\[
(\delta_i)_{\text{Bocc}} = -0.33^0Cp_z + 0.94^0Cp_x.
\]

We calculate an LFO energy $\lambda(\delta_i)$ according to eq. (27). All LFO calculation procedures were also carried out on LUMMOX. Then, a reactivity index (RI) is defined by

\[
RI = 1/|\lambda_{\text{HOMO}} - \lambda_{\text{LUMO}}| + 1/|\lambda_{\text{HOMO}} - \lambda_{\text{LUMO}}|.
\]

**Results and Discussion**

LFO energies ($\lambda$) and RIs are shown in Table 2. The order of ethylene insertion activities is $(10) > (9) > (12) > (11) > (14) > (13)$. Electron acceptability of the catalysts, $1/|\lambda_{\text{HOMO}} - \lambda_{\text{LUMO}}|$, markedly decreases in the case of catalysts having octahedral structure because of the ligand located trans to the incoming ethylene, whereas electron donerability of them, $1/|\lambda_{\text{HOMO}} - \lambda_{\text{LUMO}}|$, is little affected by the shape of the catalysts. Activities of zirconium catalysts are large compared with the corresponding titanium catalysts having same structure.

**Conclusion**

The total overlap population of all PIOs ($\Sigma OP$) is a good index for activities of polymerization catalysts. It is possible quantitatively to put in order of activities of polymerization catalysts using the RI based on LFO calculation.

LUMMOX is a simple and easy way to handle reaction simulators for developing industrial catalysts.
Table 2. LFO Energies (λ) and RIs of Ethylene Insertion on Model Chlorides and Metallocenes Catalysts (9)–(14) (eV).

| Models          | λ_{occ} | λ_{unocc} | 1/|λ_{occ} - λ_{unocc}| | 1/|λ_{occ} - λ_{unocc}| | RI |
|-----------------|---------|-----------|----------------|----------------|----------------|------|
| (9): [T_{a-CH_{3}TiCl_{2}}]^{+}/C_{2}H_{4} | -16.51  | -8.00     | 0.194          | 0.125          | 0.319          |
| (10): [T_{a-CH_{3}ZrCl_{2}}]^{+}/C_{2}H_{4} | -16.23  | -9.05     | 0.244          | 0.130          | 0.374          |
| (11): [T_{a-CH_{3}TiCp_{2}}]^{+}/C_{2}H_{4} | -16.28  | -5.59     | 0.132          | 0.129          | 0.261          |
| (12): [T_{a-CH_{3}ZrCp_{2}}]^{+}/C_{2}H_{4} | -15.91  | -7.24     | 0.169          | 0.136          | 0.305          |
| (13): [O_{a-CH_{3}TiCl_{4}}]^{-}/C_{2}H_{4} | -17.08  | +0.88     | 0.071          | 0.117          | 0.188          |
| (14): [O_{a-CH_{3}ZrCl_{4}}]^{-}/C_{2}H_{4} | -17.06  | -2.04     | 0.090          | 0.117          | 0.207          |
| C_{2}H_{4}      | -13.15  | -8.53     |               |               |               |

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