Multireference Correlated Wavefunction Calculations and Reaction Flux Analyses of Methyl Ester Combustion

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See Victor Oyeyemi’s poster today
Common biodiesel derived from rapeseed oil and soybeans:

- Methyl esters (R(C=O)OCH₃): methyl palmitate (C₁₇H₃₄O₂), stearate (C₁₉H₃₈O₂), oleate (C₁₉H₃₆O₂), linoleate (C₁₉H₃₄O₂), linolenate (C₁₉H₃₂O₂) – first two fully saturated, last three increasing number of C=C bonds

- Predict pyrolysis reaction energetics: breaking C-H, C-C, C=C, C-O, C=O bonds

- Predict kinetics of most important/most uncertain combustion reaction steps

- Compare to smaller methyl esters to test “group additivity”

- How to treat such large molecules with accurate QM? MRSDCI O(N⁶)... fast new algorithms for accurate QM.
Thermochemical Kinetics from Quantum Chemistry

- **Structure Optimization**
  - Conformation Search for Global and Statistically Favored Minima using Molecular Mechanics (Classical Force Fields)
  - Local Refinement at Hartree-Fock and/or DFT B3LYP Levels

- **Thermochemistry**
  - C-H, C-C, C-O bond dissociation energies using CASSCF/L-MRSDCI/L-MRAPCF with basis set extrapolation

- **Kinetics**
  - Reaction Flux and Sensitivity Analyses to identify most important/most uncertain reaction steps
  - DFT B3LYP determination of reaction paths/structures and zero point energies/thermal corrections
  - L-MRSDCI/MRACPF prediction of activation energies
Multireference Configuration Interaction (MRCI)

Configuration Interaction Expansion

\[ \Psi^{CI} = \sum_R c_R \Psi_R + \sum_{i,a} c_i^a \Psi_i^a + \sum_{i,j,ab} c_{ij}^{ab} \Psi_{ij}^{ab} + \sum_{i,j,k,abc} c_{ijk}^{abc} \Psi_{ijk}^{abc} \]

Solve eigenvalue equation: \( HC = EC \)

\[
\begin{bmatrix}
< \Psi_0 | H | \Psi_0 > & < \Psi_0 | H | \Psi_i^a > & \cdots & < \Psi_0 | H | \Psi_{ij}^{ab} > \\
< \Psi_i^a | H | \Psi_0 > & < \Psi_i^a | H | \Psi_i^a > & \cdots & < \Psi_i^a | H | \Psi_{ij}^{ab} > \\
\vdots & \vdots & \ddots & \vdots \\
< \Psi_{ij}^{ab} | H | \Psi_0 > & < \Psi_{ij}^{ab} | H | \Psi_i^a > & \cdots & < \Psi_{ij}^{ab} | H | \Psi_{ij}^{ab} > \\
\end{bmatrix}
\begin{bmatrix}
c_0 \\
c_i^a \\
\vdots \\
c_{ij}^{ab} \\
\end{bmatrix} = E
\begin{bmatrix}
c_0 \\
c_i^a \\
\vdots \\
c_{ij}^{ab} \\
\end{bmatrix}
\]

Conventional scaling of electronic structure methods

<table>
<thead>
<tr>
<th>Method</th>
<th>Scaling</th>
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<th>Scaling</th>
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</thead>
<tbody>
<tr>
<td>HF</td>
<td>O(N⁴)</td>
<td>CCSD</td>
<td>O(N⁶)</td>
</tr>
<tr>
<td>KS-DFT</td>
<td>O(N³)</td>
<td>CCSD(T)</td>
<td>O(N⁷)</td>
</tr>
<tr>
<td>MP2</td>
<td>O(N⁵)</td>
<td>MRSDCI</td>
<td>O(N⁶)</td>
</tr>
<tr>
<td>MP4</td>
<td>O(N⁷)</td>
<td>FCI</td>
<td>O(N!)</td>
</tr>
</tbody>
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Linear scaling of 2008 PAO/IS algorithm lost (CD is $O(N^{2-3})$ scaling) but prefactor much lower
⇒ larger molecules (~50 heavy atoms) accessible w/ no loss of accuracy ($\mu$Hartree error)

However, CI is not size-extensive ⇒ error grows with system size...

L-MRSDCI-IS BREAKS BONDS SMOOTHLY AND ACCURATELY: SCREENING RETAINS µH ACCURACY; LMRSDCI RECOVERS >98% CORR.

PES along the reaction coordinate for bond cleavage along the C=C bond in trans-6-dodecene ($C_{12}H_{24}$). Inset shows an expanded view of the curves.
Basis Set Extrapolation

- **Dunning-type basis sets**: correlation-consistent basis sets designed for extrapolation to the complete basis set (CBS) limit
  - cc-pVXZ where X=D, T, Q, 5, 6, for a sequence of added angular momentum functions
  - Computational cost limits the maximum cardinal number (X)

- **A Dual-Cardinal Extrapolation Scheme**:
  - CASSCF energies and correlation energies are separately extrapolated
  
  \[ E_{tot} = E^{\text{CASSCF}} + E^{\text{cor}} \]

  - A power law scheme proposed by Truhlar
  
  \[
  E_X^{\text{CASSCF}} = E_\infty^{\text{CASSCF}} + A^{\text{CASSCF}} x_\infty^{-\alpha} \quad \alpha = 3.4^* \\
  E_X^{\text{cor}} = E_\infty^{\text{cor}} + A^{\text{cor}} x_\infty^{-\beta} \quad \beta = 2.4^{**} 
  \]

  * Optimized for HF
  ** Optimized for CCSD

Consider largest surrogate for biodiesel for which combustion mechanism available. Reduced methyl decanoate mechanism used as input to Chemkin-Pro ... (Help from Ju and Green groups greatly appreciated!)

- Reaction flux analysis of reduced combustion mechanism* for methyl decanoate at both low and high temperature to find main pathways.
  - $\beta$-scission reactions important at both high and low temperature.
  - Addition of $O_2$ produces a more complex mechanism at low temperature. Isomerization and decomposition of these species need more accurate data.

- Sensitivity analysis performed to determine the sensitive reactions under adiabatic conditions at 650-1200 K.
  - Reactions of large molecule/radicals such as MD at low temperature are more sensitive than at high temperature.
  - Hydrogen abstraction reactions from large molecules sensitive at all temperatures.
  - A-factor sensitivity for concentrations of species is found to be small in general.

Connection to other C-EFRC Team Members and Expected Impact

- **Theory connections:**
  - Don Truhlar – calculation of VTST rate constants using LMRSDCI barriers/energetics as input
  - Steve Klippenstein/Jim Miller – input for high pressure kinetics
  - Bill Green – building/refinement of overall kinetic models
  - ASCR collaboration with Mark Gordon to parallelize LMRSDCI code

- **Experimental connections:**
  - Fred Dryer – flow reactor studies
  - Fokion Egolfopoulos – counterflow flame studies
  - Yiguang Ju – jet stirred reactor/PIV/LIF/molecular beam MS

- **Expected Impact:**
  - Understanding of biodiesel molecule combustion reactions as a function of temperature and pressure.