Application of Local Coupled-Cluster Methods to Enzymatic Reactivity

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Computational Chemistry and Biochemistry
The LMOMO method

- CCSD(T) : $O(N^7)$ scaling of the computational cost
- Towards sub-linear scaling:
  - localization of occupied and virtual orbital spaces
  - grouping of orbitals into regions of interest (active site vs. environment)
  - application of different levels of theory
LMP2 vs. LCCSD(T0)

Optimization with DFT/BP86 and triple-ζ STO basis set with polarization functions. Single points with cc-pVTZ and for Mo aug-cc-pVTZ and ECP28MDF.
Results - Region Calculations

<table>
<thead>
<tr>
<th></th>
<th>LMP2</th>
<th>LCCSD(T0):LMP2</th>
<th>LCCSD(T0)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R1</td>
<td>R2</td>
<td>R3</td>
</tr>
<tr>
<td>RS</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>TS1</td>
<td>90.1</td>
<td>-16.7</td>
<td>-6.2</td>
</tr>
<tr>
<td>IM1</td>
<td>-68.3</td>
<td>-160.1</td>
<td>-158.2</td>
</tr>
<tr>
<td>TS2</td>
<td>65.7</td>
<td>-21.7</td>
<td>-19.2</td>
</tr>
<tr>
<td>PS</td>
<td>55.6</td>
<td>-33.4</td>
<td>-31.5</td>
</tr>
<tr>
<td>RMSD</td>
<td>78.6</td>
<td>6.5</td>
<td>1.7</td>
</tr>
</tbody>
</table>

All energies are in kJ/mol.
Timings

R1

\[ \text{H}_3\text{C} \]
\[ \text{S} \]
\[ \text{Mo} \]
\[ \text{O} \]
\[ \text{S} \]
\[ \text{O} \]
\[ \text{R} \]
\[ \text{O} \]
\[ \text{O} \]
\[ \text{H}_3\text{C} \]

\( n = 15 \)

R2

\[ \text{H}_3\text{C} \]
\[ \text{S} \]
\[ \text{Mo} \]
\[ \text{O} \]
\[ \text{S} \]
\[ \text{O} \]
\[ \text{R} \]
\[ \text{O} \]
\[ \text{O} \]
\[ \text{H}_3\text{C} \]

\( n = 27 \)

R3

\[ \text{H}_3\text{C} \]
\[ \text{S} \]
\[ \text{Mo} \]
\[ \text{O} \]
\[ \text{S} \]
\[ \text{O} \]
\[ \text{R} \]
\[ \text{O} \]
\[ \text{O} \]
\[ \text{H}_3\text{C} \]

\( n = 33 \)

n = 97

REAL Time [min]

LCCSD(T0):LMP2

\( n \) (number of orbitals in high level region)

0 20 40 60 80 100

100 900 800 700 600 500 400 300 200 100

n


Open Shell Applications

- Benchmark set
- 12 complexation reactions

![Benchmark set](image)

- LUCSD(T0):LRMP2

![Graph](image)
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