Linear-Scaling Quantum Chemistry:

Multilayer

Divide-Expand-Consolidate (DEC) Scheme

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The Multilayer DEC Scheme
The Multilayer DEC (ML-DEC) Scheme

Small region of interest within larger system

More time spent on fragments that don’t make a strong contribution to property of interest

Take advantage of independent nature of fragments
The ML-DEC Scheme

- Example: Region of interest centered on P
  - Q, S evaluated at RI-MP2 level
  - P evaluated at CCSD level

- Intent is to capture important correlation contributions in region of interest – accurate energy differences

- Suited for local effects: adsorption, defect sites, catalytically active sites, etc.

P, Q, S = optimized fragments
The ML-DEC Scheme

- User defines high and low level layers in input file and assigns atoms to each.
- All fragments optimized at RI-MP2 level of theory

<table>
<thead>
<tr>
<th>Low Level</th>
<th>RI-MP2</th>
<th>CCSD</th>
<th>CCSD(T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RI-MP2</td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>CCSD</td>
<td></td>
<td></td>
<td>X</td>
</tr>
</tbody>
</table>

- After optimization, atomic fragments assigned to user-specified level of theory.
- Pair fragments are evaluated at the higher level of the two atomic fragments:
  - 1-2: CC\textsubscript{high}
  - 2-4: CC\textsubscript{high}
  - 3-4: CC\textsubscript{low}
- Pair estimates at RI-MP2 level determine if pair level is reduced (not skipped).

Layers not required to be contiguous – e.g. multi-site catalysis
The ML-DEC Scheme

- Special consideration for HF/RI-MP2:
  - Only optimize low-level atomic fragments that contribute to high-level pairs

- Unoptimized atomic fragments automatically excluded from pairs
  - 2-3: RI-MP2
  - 2-4: HF
  - 3-4: HF

$R_{\text{thr}}$
(recommended: 10 Å)
- Atomic fragments within $R_{\text{thr}}$ of any high-level atom are optimized, otherwise skipped

<table>
<thead>
<tr>
<th></th>
<th>RI-MP2</th>
<th>CCSD</th>
<th>CCSD(T)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>High Level</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HF</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RI-MP2</td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>CCSD</td>
<td></td>
<td></td>
<td>X</td>
</tr>
</tbody>
</table>

$R_{\text{thr}}$

$\text{d} < R_{\text{thr}}$

$\text{d} > R_{\text{thr}}$
The ML-DEC Scheme: Summary

Local HF orbitals → Atomic fragment optimization → Pair fragments (pair distance < $R_{th}$) → Collection of results for energy and density

Performed at RI-MP2 level for all fragments

\[ P = \text{Occupied orbital space} \]
\[ [P] = \text{Virtual orbital space} \]

\[ E_P = \sum_{i \in P, j \in P} (t_{ij}^{ab} + t_{i}^{a} t_{j}^{b})(2g_{iajb} - g_{ibja}) \]

Performed at target level

\[ \Delta E_{PQ} = \sum_{i \in P, j \in Q} (t_{ij}^{ab} + t_{i}^{a} t_{j}^{b})(2g_{iajb} - g_{ibja}) + P \leftrightarrow Q \text{ term} \]

\[ E_{corr} = E_{corr,\text{high}} + E_{corr,\text{low}} \]

Test Case: Palmitic Acid Dimer

Palmitic acid dimer 
cc-pVTZ, FOT=10^{-4} 
1976 basis functions

HF/RIMP2, 10.0 Å cutoff

<table>
<thead>
<tr>
<th>Model</th>
<th>Nproc</th>
<th>RI-MP2 frags</th>
<th>Wall time (min)</th>
<th>$E_{\text{corr}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEC monomer</td>
<td>7</td>
<td>17*, 51</td>
<td>17.51</td>
<td>-3.241(3)</td>
</tr>
<tr>
<td>ML-DEC monomer</td>
<td>7</td>
<td>9*, 6</td>
<td>6.71</td>
<td>-1.534(2)</td>
</tr>
<tr>
<td>DEC dimer</td>
<td>33</td>
<td>36*, 130</td>
<td>10.19</td>
<td>-6.493(7)</td>
</tr>
<tr>
<td>ML-DEC dimer</td>
<td>33</td>
<td>20*, 32</td>
<td>5.51</td>
<td>-3.084(4)</td>
</tr>
</tbody>
</table>

*Atomic fragment optimization

$$\Delta E_{\text{HF/RI-MP2}} = -0.033$$

$$\Delta E_{\text{RI-MP2}} = -0.027$$
Test Case: Palmitic Acid Dimer

Palmitic acid dimer
cc-pVTZ, FOT=10^-4
1976 basis functions

HF/RI-MP2

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<table>
<thead>
<tr>
<th>Monomer, 988 basis functions</th>
<th>Dimer, 1976 basis functions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>Fragment</td>
</tr>
<tr>
<td>Optimizations</td>
<td>Energy</td>
</tr>
<tr>
<td>ML-DEC</td>
<td>9</td>
</tr>
<tr>
<td>ML-DEC (ext₁)</td>
<td>10</td>
</tr>
<tr>
<td>ML-DEC (ext₂)</td>
<td>11</td>
</tr>
<tr>
<td>DEC-RI-MP2</td>
<td>17</td>
</tr>
</tbody>
</table>
Test Case: Palmitic Acid Dimer

Palmitic acid dimer
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1976 basis functions

HF/RI-MP2

- Even with smallest high level layer, interaction energies agree within FOT.
- Agreement converges to standard DEC RI-MP2 energy as high level is increased.

<table>
<thead>
<tr>
<th>Model</th>
<th>$TTS_m$ (min)</th>
<th>$TTS_d$ (min)</th>
<th>$\Delta E$ ($E_h$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ML-DEC</td>
<td>6.71</td>
<td>5.51</td>
<td>-0.033 (5)</td>
</tr>
<tr>
<td>ML-DEC (ext₁)</td>
<td>7.98</td>
<td>6.21</td>
<td>-0.026 (5)</td>
</tr>
<tr>
<td>ML-DEC (ext₂)</td>
<td>9.27</td>
<td>6.84</td>
<td>-0.027 (6)</td>
</tr>
<tr>
<td>DEC-RI-MP2</td>
<td>17.51</td>
<td>10.19</td>
<td>-0.027 (8)</td>
</tr>
</tbody>
</table>
Test Case: Palmitic Acid Dimer

Palmitic acid dimer cc-pVDZ, FOT=10^{-4} 824 basis functions

RI-MP2/CCSD

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<tr>
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<th>Nproc</th>
<th>CCSD frags</th>
<th>Wall time (h)</th>
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</tr>
</thead>
<tbody>
<tr>
<td>DEC monomer</td>
<td>129</td>
<td>76</td>
<td>3.21</td>
<td>-2.853(3)</td>
</tr>
<tr>
<td>ML-DEC monomer</td>
<td>129</td>
<td>14</td>
<td>0.24</td>
<td>-2.655(3)</td>
</tr>
<tr>
<td>DEC dimer</td>
<td>129</td>
<td>164</td>
<td>8.4</td>
<td>-5.712(7)</td>
</tr>
<tr>
<td>ML-DEC dimer</td>
<td>129</td>
<td>38</td>
<td>1.85</td>
<td>-5.316(7)</td>
</tr>
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\[
\Delta E_{\text{RI-MP2/CCSD}} = -0.027
\]

\[
\Delta E_{\text{CCSD}} = -0.026
\]
Application: Acid gas adsorption in Mg-MOF-74
MOFs for CO$_2$ Capture

High uptake in many MOFs with OMSs (e.g. Mg-MOF-74, HKUST-1)

Non-N$_2$ flue gas components

- CO$_2$: 61.65%
- O$_2$: 13.92%
- H$_2$O: 23.86%
- SO$_x$ + NO$_x$: 0.52%
MOFs for CO$_2$ Capture

Non-N$_2$ flue gas components

- CO$_2$: 61.65%
- H$_2$O: 23.86%
- O$_2$: 13.92%
- SO$_x$ + NO$_x$: 0.52%
- Other: 0.05%

Competitors, Strong binding to MOF OMSs → Lead to degradation of MOFs
Modeling Acid Gas adsorption in Mg-MOF-74

- Plane-wave DFT
  - Results depend on choice of functional, Hubbard U corrections, dispersion corrections etc.

- Small cluster models
  - Suffer from finite size effects. Clusters large enough to replicate environment within the bulk MOF are too expensive for CC.

- Desire to model large finite MOF clusters at CC level of theory while capturing bulk MOF environment.
  - Local interaction – good candidate for ML-DEC scheme.
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## Mg-MOF-74 + CO$_2$

### HF/RI-MP2

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<th>Wall time (h)</th>
<th>$E_{\text{corr}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEC MOF</td>
<td>65</td>
<td>76*, 633</td>
<td>3.06</td>
<td>-16.131(15)</td>
</tr>
<tr>
<td>ML-DEC MOF</td>
<td>65</td>
<td>76*, 135</td>
<td>2.26</td>
<td>-12.876(15)</td>
</tr>
<tr>
<td>DEC MOF+CO$_2$</td>
<td>65</td>
<td>78*, 689</td>
<td>3.78</td>
<td>-16.745(16)</td>
</tr>
<tr>
<td>ML-DEC MOF+CO$_2$</td>
<td>65</td>
<td>78*, 184</td>
<td>2.84</td>
<td>-13.502(16)</td>
</tr>
</tbody>
</table>

* *Atomic fragment optimization

$$\Delta E_{\text{HF/RI-MP2}} = -0.033$$  
$$\Delta E_{\text{RI-MP2}} = -0.022$$
Mg-MOF-74 + SO$_2$/H$_2$O

Interaction energy ($E_h$)

<table>
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<tr>
<th>Gas</th>
<th>HF/RI-MP2</th>
<th>RI-MP2</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_2$</td>
<td>0.028(16)</td>
<td>-0.029(16)</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>-0.099(16)</td>
<td>-0.038(16)</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>-0.033(16)</td>
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Mg-MOF-74 + SO$_2$/H$_2$O

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Target system: MOF channel

- HF/RI-MP2 to optimize high level layer.
- RI-MP2/CCSD for final interaction energy calculations.

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<tr>
<th>Model</th>
<th>Fragment Optimizations</th>
<th>Pair Energy Calculations</th>
</tr>
</thead>
<tbody>
<tr>
<td>ML-DEC</td>
<td>202</td>
<td>201</td>
</tr>
<tr>
<td>ML-DEC (ext₁)</td>
<td>484</td>
<td>510</td>
</tr>
<tr>
<td>DEC-RI-MP2</td>
<td>568</td>
<td>7002</td>
</tr>
</tbody>
</table>

Most important for HF/RI-MP2: ML-DEC (ext₁) Most important for RI-MP2/CCSD: DEC-RI-MP2

cc-pVDZ
~10,000 basis functions
Targeting Performance on Summit

- LSDalton makes use of MPI, OpenMP, and OpenACC.
  - Linear scaling as long as problem is big enough

- RI-MP2 modules already include OpenACC acceleration
  - jsrun -n 6 -a 1 -g 1 -r 6 -c 7 -brs
  - >2x speedup using 1 GPU/rs compared to 0 GPUs/rs

- Current efforts focus on integration with the TAL-SH tensor algebra library for GPU-acceleration of CC modules (https://github.com/DmitryLyakh/TAL_SH)
GPU Offloading of Tensor Contractions with TAL-SH

• CC calculations require evaluation of tensor contractions. Efficient handling of these contractions is key to good performance of these modules.

• Currently utilizing ScaTeLib: a Scalable Tensor Library in order to distribute tensor contractions across multiple ranks via tiling.

• E.g.: $$C_{ijkl} = \alpha \sum_{a,b} A_{ajlb} B_{kba} + \beta C_{ijkl}$$
  - A and B must be sorted appropriately: $$A_{ajlb} \Rightarrow A_{jlab}, B_{kba} \Rightarrow B_{abki}$$
  - Call dgemm
  - Returns contribution to local C tile as $$C_{ijkl}$$. Reorder $$\Rightarrow C_{ijkl}$$ and add to local tile.
GPU Offloading of Tensor Contractions with TAL-SH

- TAL-SH: Tensor Algebra Library for Shared-memory systems. Integrated as backend for ScaTeLib.
GPU Offloading of Tensor Contractions with TAL-SH

- **TAL-SH**: Tensor Algebra Library for Shared-memory systems. Integrated as backend for ScaTeLib.

- Handles sorting, no explicit reorder calls necessary in ScaTeLib

- Asynchronous task scheduling

- Tasks are pipelined to overlap computation and data transfer
  - 2 active tasks per GPU at any time

- Basic implementation provides ~2.25x speedup for contraction of two 4th-order tensors with tile size of 80 (Titan).
GPU Offloading of Tensor Contractions with TAL-SH

- TAL-SH: Tensor Algebra Library for Shared-memory systems. Integrated as backend for ScaTeLib.

- Targeted performance improvements:
  - OpenMP compatibility
  - Reduction of data transfer
  - Optimization of tile sizes used within LSDalton
    - Ensure time spent in data transfer < time spent in computation
Acknowledgements

Dmytro Bykov: LSDALTON CAAR Liason

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