Fragmentation methods
Scaling of QM Methods

- HF, DFT scale as $N^4$
- MP2 scales as $N^5$
- CC methods scale as $N^7$
- What if we could “freeze” the value of $N$ regardless of the size of the system? Then each method would scale linearly with respect to the system size. This is the goal of fragmentation methods.

*(where $N$ is a measure of system size such as the number of basis functions)*
Fragmentation Methods

• Biomolecules contain hundreds or thousands of atoms, making accurate quantum calculations either very difficult or impossible

• Quantum Mechanics/Molecular Mechanics (QM/MM) methods have become popular in recent years, however,

  • As system size grows the QM region can get unwieldy

  • The energy contribution from the environment becomes too large to obtain reasonable accuracy from molecular mechanics

Fragmentation methods offer a unique solution to accurate calculations on large molecules
Background & Motivations

- Fragmentation methods can be divided into two groups, one-step and two-step

- One-step methods obtain the energy and properties directly from fragment calculations. Methods included are:
  - X-pol, FMO, KEM, MFCC, SFM (SMF) and MTA

- Two-step methods first compute some total property, for example the density, from fragment calculations. Other properties such as the total energy are then evaluated from the total property obtained in the first step. Examples of two-step methods are:
  - X-Pol-X, MFCC-DM and DC

• Division of methods can be further refined into one-body, many-body and conglomerate methods.
  • one-body methods do not perform any “higher order” QM many-body calculations
  • many-body methods include pairs, triples etc QM corrections to the one-body methods
  • conglomerate methods use other means to obtain many-body corrections (SFM/SMF)
The Fragment Molecular Orbital (FMO) Method:

Kitaura et al.: CPL, 313, 701 (1999)

- Exchange and self-consistency are local in most molecules
- Treat non-local parts using just the Coulomb operator, thereby ignoring exchange
- Perform the molecular calculations individually in the rigorous Coulomb field of the whole system
- Improved by explicit many-body corrections for pairs and triples (dimers & trimers)
- The Coulomb bath allows for fragmentation without hydrogen capping

\[ x = \text{monomer} \]

Coulomb “bath” of the full system being taken into account

monomer electron density being calculated
The Fragment Molecular Orbital Method

- Bonds are fractioned electrostatically
- Electrons are assigned heterolytically
- FMO fragmentation should be conducted based upon chemical knowledge (not a formal “mathematical exercise”)
- Hydrogen bonding is accounted for by explicit dimer (fragment pair) calculations
- Dimer & trimer (fragment triple) calculations allow for other quantum effects to be taken into account
In molecular clusters, fragmentation is easier, requiring no covalent bond breaking.

We can have one molecule per fragment, two molecules per fragment etc.

For covalently bonded molecules, we divide the fragment into pieces so as not to destroy bond electron pairs.
The total energy of the system can be written as

\[ E = \sum_{i=1}^{N} E_i + \sum_{i<j}^{N} (E_{ij} - E_i - E_j) \\
+ \sum_{i<j<k}^{N} \{ (E_{ijk} - E_i - E_j - E_k) - (E_{ij} - E_i - E_j) \\
- (E_{jk} - E_j - E_k) - (E_{ki} - E_k - E_i) \} + \cdots, \]

Where the monomer (I), dimer (IJ) and trimer (IJK) energies are obtained using the SCF method with modified Fock operators.
The Fragment Molecular Orbital Method

1. Divide molecule into fragments and assign electrons to these fragments

2. Calculate initial electron density distribution of the fragments in the Coulomb “bath” of the full system

3. Construct the individual fragment Fock operators using the densities calculated in 2 and solve for the fragment energies

4. Determine if the density has converged for all the fragments. If not, go back to step 3

5. Construct Hamiltonians for each dimer (trimer) calculation using the converged monomer densities from steps 3-4

6. Calculate total energy and electron density
Steps 1-3:
Coulomb “bath” of the full system being taken into account

Steps 4:
Steps 1 through 3 are looped until the density of the full system converges to some predetermined threshold

Steps 5-6:
Converged Coulomb “bath” of the full system from monomer SCF
dimer (trimer) electron density being calculated in the presence of the converged ESP
each dimer (trimer) calculation is performed once
The Fragment Molecular Orbital Method

The number of dimer calculations increases as "n choose 2" where n is the number of fragments.

7 fragments = 21 dimers
8 fragments = 28 dimers
16 fragments = 120 dimers
32 fragments = 496 dimers
64 fragments = 2016 dimers
128 fragments = 8128 dimers

The total number of dimer calculations increases rapidly!

Two solutions: Approximations and parallelization
The Fragment Molecular Orbital Method: Approximations

\[ R_{IJ} = \min_{i \in I, j \in J} \left\{ \frac{\left| \vec{r}_i - \vec{r}_j \right|}{r_i^{\text{vib}} + r_j^{\text{vib}}} \right\} \]

User defined cut-off value \( R_{\text{cut}} \)

\[ E_{\text{FMO}}^2 = \sum_I E_I + \sum_{I \neq J}^{R_{\text{cut}}} \Delta E_{IJ} + \sum_{I \neq J}^{R_{\text{cut}}} \Delta E_{IJ}^{\text{sep}} \]
• The Generalized Distributed Data Interface (GDDI)

• GDDI allows for massively parallel calculations on clusters of computers or supercomputers
  
  • After the molecule is divided into fragments, each fragment is sent to a group which is composed of more than one processor or SMP enclosure
  
  • Each fragment is then run in parallel in each group
  
  • This provides two levels of parallelization, greatly speeding up the calculation
The Fragment Molecular Orbital Method: Parallelization
The Fragment Molecular Orbital Method

- FMO has all of the following wavefunction types implemented
  - RHF, ROHF, DFT/TDDFT, MP2, CC, CIS and MCSCF (all of which support FMO3 except MCSCF)
  - FMO also has a multilayer implementation allowing you to specify different levels of electron correlation or basis sets in different layers
  - FMO is also interfaced with PCM and EFP for solvent effects
  - RUNTYPs available are ENERGY, GRADIENT, OPTIMIZE and GLOBOP
The Fragment Molecular Orbital Method - Examples

32-WATER CLUSTERS

MP2
Cluster Binding Energies

FMO2 Binding Energy per molecule (kcal/mol)

Fully ab initio Binding Energy per molecule (kcal/mol)
32-WATER CLUSTERS

The Fragment Molecular Orbital Method - Examples
Heterogeneous Catalysis on MSN

Gatekeeper groups selectively allow reactants "A" (not "B") to enter and form product "P"
Mesoporous Silica Nanoparticle (MSN)

1770 atoms
Diffusion Through MSN Pore

RC-A  RC-B  RC-C

FMO/HF  FMO/HF-D
Hydrated cisplatin-DNA complex. FMO2-MP2 calculations were performed using the MCP model.

Sodium ions and water molecules were relaxed with the Amber99 force field.

This calculation included:

- 3596 atoms
- \(~997\) fragments
The Fragment Molecular Orbital Method - Examples: Ionic Liquid

FMO2-MP2/6-31G(d) optimized* octamer structure (red) overlaid with \textit{ab initio} MP2/6-31G(d) optimized structure (yellow)

MP2 optimization took 105 geometry steps and \~63 hours

FMO2-MP2 optimization took 94 geometry steps and \~5.5 hours

\*Optimizations performed on 256 CPUs of an IBM Power6 cluster with 32 CPUs per node and 2 GB of RAM per CPU. GDDI was used for FMO2 calculation with one node per GDDI group.

Error = -2.23 kcal/mol
RMSD = 0.04 angstroms
<table>
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<tr>
<th># Groups</th>
<th># CPUs</th>
<th>CPU time (min)</th>
<th>Wall time (min)</th>
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<td>1103</td>
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<td>16</td>
<td>512</td>
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<td>32</td>
<td>1024</td>
<td>299</td>
<td>430</td>
</tr>
<tr>
<td>48</td>
<td>1536</td>
<td>210</td>
<td>415</td>
</tr>
</tbody>
</table>

*4.7 GHz IBM Power6 processors with 2GB of RAM per CPU and 32 CPUs per node

FMO2-MP2 single point energy calculation
6-31G(d) basis set
855 fragments (one residue per fragment)
13625 atoms

ZVDA protein from the PDB database
Cell 131 (2007) 756-769

The Fragment Molecular Orbital Method - Examples
The Fragment Molecular Orbital Method - Examples

- 124 amino acid residues
- 3460 water molecules
- one residue or water per fragment
- FMO2-MP2/6-311G(d,p) energy calculation
- 131,432 basis functions
- 16,384 nodes (262,144 cores)
- ~10 hours
- ~72% of Blue Waters
The Fragment Molecular Orbital Method
Timings: Water Clusters

<table>
<thead>
<tr>
<th>Cluster Size</th>
<th>Wall Clock Time (seconds)</th>
<th>Wall Clock Time (seconds)</th>
<th>Error (kcal/mol)</th>
<th>Wall Clock Time (seconds)</th>
<th>Error (kcal/mol)</th>
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</thead>
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<td>16</td>
<td>394</td>
<td>10</td>
<td>2.95</td>
<td>81</td>
<td>0.71</td>
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<tr>
<td>20</td>
<td>1119</td>
<td>11</td>
<td>4.66</td>
<td>141</td>
<td>0.17</td>
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<tr>
<td>32</td>
<td>9989</td>
<td>20</td>
<td>11.80</td>
<td>429</td>
<td>2.21</td>
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</table>

Each calculation was run on 6 nodes containing two 2.66 GHz Intel quad core Xeon processors (48 CPUs total) and 16 GB of RAM. For the FMO calculations, GDDI was used with each node specified as a group (6 groups total).

48 cores with 2 GB of RAM per core was the minimum computational requirement for the fully ab initio 32 water calculation.
FMO2-MP2/aug-cc-pVDZ gradients:

**BG/P: ANL (Graham Fletcher)**

<table>
<thead>
<tr>
<th>Racks:</th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>18</th>
<th>32</th>
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<tbody>
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<td>32,768</td>
<td>65,536</td>
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<tr>
<td>Basis</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Waters</td>
<td>Atoms</td>
<td>Functions</td>
<td>Wall Time (minutes)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>-----------</td>
<td>--------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>128</td>
<td>384</td>
<td>5504</td>
<td>8.6</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>256</td>
<td>768</td>
<td>11,008</td>
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<tr>
<td>512</td>
<td>1536</td>
<td>22,016</td>
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<td>44,032</td>
<td>41.1</td>
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</tr>
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</table>

### The Fragment Molecular Orbital Method

#### Timings: Ionic Liquids

<table>
<thead>
<tr>
<th>1-H,4-H-1,2,4-triazolium dinitramide octamer</th>
<th>Timing* (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6-31++G(d,p)</td>
</tr>
<tr>
<td>#CPUs</td>
<td>FMO2-MP2</td>
</tr>
<tr>
<td>4</td>
<td>42.9</td>
</tr>
<tr>
<td>8</td>
<td>22.3</td>
</tr>
<tr>
<td>16</td>
<td>11.4</td>
</tr>
<tr>
<td>32</td>
<td>5.8</td>
</tr>
<tr>
<td>64</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Full ab initio MP2 calculation requires ~77 GB of RAM
FMO2-MP2 calculation requires less than 1 GB of RAM

Error = 0.67 kcal/mol

* Timings for ionic liquid clusters performed on a computer cluster containing 2.66GHz Intel Xeon processors.
  Each node contains two 4 core CPUs and 16 GB of RAM.
  GDDM division was across individual nodes (1 group = 8 CPUs)
The Fragment Molecular Orbital Method - Memory Requirements

CCSD(T)/aug-cc-pVQZ single point energy calculation on a cluster of six water molecules

<table>
<thead>
<tr>
<th></th>
<th>64 cores</th>
<th>64 cores</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8 cores/node</td>
<td>1 core/node</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>80 GB RAM per node</td>
<td>32 GB RAM per node</td>
</tr>
<tr>
<td>FMO3-CC</td>
<td>12 GB RAM per node</td>
<td>4 GB RAM per node</td>
</tr>
</tbody>
</table>

*One water molecule per FMO fragment*

CCSD(T)/aug-cc-pVQZ single point energy calculation on a cluster of six argon atoms

<table>
<thead>
<tr>
<th></th>
<th>64 cores</th>
<th>64 cores</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8 cores/node</td>
<td>1 core/node</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>36 GB RAM per node</td>
<td>19 GB RAM per node</td>
</tr>
<tr>
<td>FMO2-CC</td>
<td>9 GB RAM per node</td>
<td>4 GB RAM per node</td>
</tr>
</tbody>
</table>

*Two argon atoms per FMO fragment (total of three fragments)*
# The Fragment Molecular Orbital Method

## Memory Requirements

Memory requirements per node (in GB) for fully *ab initio* CCSD(T)/6-31++G(d,p) energy calculation on hexamer cluster

<table>
<thead>
<tr>
<th>Total # of CPUs</th>
<th>Number of Cores per Node</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>643</td>
</tr>
<tr>
<td>2</td>
<td>381 643</td>
</tr>
<tr>
<td>4</td>
<td>250 381 644</td>
</tr>
<tr>
<td>8</td>
<td>185 250 382 645</td>
</tr>
<tr>
<td>16</td>
<td>152 185 251 384 648</td>
</tr>
<tr>
<td>32</td>
<td>136 152 186 253 386</td>
</tr>
<tr>
<td>64</td>
<td>127 136 153 187 255</td>
</tr>
<tr>
<td>128</td>
<td>123 128 137 154 190</td>
</tr>
</tbody>
</table>

Memory requirements per node (in GB) for FMO2-CCSD(T)/6-31++G(d,p) energy calculation on any size cluster

<table>
<thead>
<tr>
<th>Total # of CPUs</th>
<th>Number of Cores per Node</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>5 9</td>
</tr>
<tr>
<td>4</td>
<td>4 5 9</td>
</tr>
<tr>
<td>8</td>
<td>3 4 5 9</td>
</tr>
<tr>
<td>16</td>
<td>2 3 4 6 9</td>
</tr>
<tr>
<td>32</td>
<td>2 2 3 4 6</td>
</tr>
<tr>
<td>64</td>
<td>2 2 3 3 4</td>
</tr>
<tr>
<td>128</td>
<td>2 2 3 3 3</td>
</tr>
</tbody>
</table>
The Effective Fragment Potential Method

Originally developed to describe aqueous solvent effects on molecules of biological interest.

The EFP method is an ab initio based model potential for the evaluation of intermolecular forces.

Each molecule is represented as a fragment of fixed geometry with a set of parameters derived from ab initio calculations.

In the original implementation (EFP1 - only water) the interaction energy between fragments consists of three terms: Coulomb, polarization and exchange repulsion.

\[ E_{EFP1}^{EFP} = E_{Coul} + E_{pol} + E_{exrep} \]

\[ E_{EFP2}^{EFP} = E_{Coul} + E_{pol} + E_{disp} + E_{exrep} + E^{ct} \]
The Effective Fragment Molecular Orbital Method

The EFMO method was developed to integrate the FMO and EFP methods in an effort to provide a generally applicable, accurate and efficient approach to large molecular systems.

(FMO fragmentation) + (EFP interactions) + (other modifications) = EFMO

\[ E_{\text{FMO}}^2 = \sum I E_I + \sum_{I,J} R_{I,J} \Delta E_{IJ} + \sum_{I,J} \Delta E_{IJ}^{\text{exp}} \]

\[ E_{\text{EFP}}^2 = E_{\text{Coul}} + E_{\text{pol}} + E_{\text{disp}} + E_{\text{exrep}} + E_{\text{ct}} \]

\[ E_{\text{EFMO}} = \sum I E_I^0 + \sum_{I,J} (\Delta E_{IJ}^0 - E_{IJ}^{\text{pol}}) + \sum_{I,J} E_{IJ}^{\text{Coul}} + E_{\text{tot}}^{\text{pol}} \]
The Effective Fragment Molecular Orbital Method

\[ E^{\text{EFMO}} = \sum_j E^0_j + \sum_{i \neq j}^{R_{ij} < R_{cut}} (\Delta E_{ij}^0 - E_{ij}^{\text{pol}}) + \sum_{i \neq j}^{R_{ij} > R_{cut}} E_{ij}^{\text{Coul}} + E_{ij}^{\text{pol}} \]

The use of isolated fragment energies eliminates the need to calculate the ESP used in standard FMO method calculations.

The many-body interaction energy formerly computed using the ESP is replaced by the total EFP polarization energy.

However, the lack of dispersion limits the EFMO method to HF and DFT calculations.

Additional computational savings could be achieved by reducing the value of \( R_{\text{cut}} \).
The Effective Fragment Molecular Orbital Method: Fully Integrated

The original formulation of the total EFMO energy was fully integrated to include all five components of the EFP energy.

\[
E_{\text{EFMO}} = \sum_I E_I^0 + \sum_{I \neq J}^{R_{I, J} \leq R_{\text{cut}}} (\Delta E^0_{IJ} - E_{IJ}^\text{pol}) + \sum_{I \neq J}^{R_{I, J} > R_{\text{cut}}} E_{IJ}^\text{Coul} + E_{IJ}^\text{pol}
\]

By including all intermolecular interactions, the user defined cut-off value \( R_{\text{cut}} \) can be reduced to neglect additional QM dimers.

The reduction in QM dimers lowers the computational requirements of FIEFMO calculations relative to standard FMO method calculations.
The Effective Fragment Molecular Orbital Method

Average total number of separated and QM dimers

<table>
<thead>
<tr>
<th>$R_{cut}$</th>
<th>8 waters separated</th>
<th>8 waters QM separated</th>
<th>16 waters separated</th>
<th>16 waters QM separated</th>
<th>32 waters separated</th>
<th>32 waters QM separated</th>
<th>64 waters separated</th>
<th>64 waters QM separated</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>28</td>
<td>0</td>
<td>120</td>
<td>0</td>
<td>496</td>
<td>0</td>
<td>2016</td>
<td>0</td>
</tr>
<tr>
<td>0.8</td>
<td>16</td>
<td>12</td>
<td>93</td>
<td>27</td>
<td>444</td>
<td>52</td>
<td>1904</td>
<td>112</td>
</tr>
<tr>
<td>1.4</td>
<td>5</td>
<td>23</td>
<td>65</td>
<td>55</td>
<td>363</td>
<td>133</td>
<td>1730</td>
<td>286</td>
</tr>
<tr>
<td>2.0</td>
<td>0</td>
<td>28</td>
<td>30</td>
<td>90</td>
<td>237</td>
<td>259</td>
<td>1418</td>
<td>598</td>
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</tbody>
</table>
## The Effective Fragment Molecular Orbital Method

### Average Signed Errors (kcal/mol)

<table>
<thead>
<tr>
<th></th>
<th>8 water molecules</th>
<th>32 water molecules</th>
</tr>
</thead>
<tbody>
<tr>
<td>R cut</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>FMO2</td>
<td>FIEFMO</td>
</tr>
<tr>
<td>0.6</td>
<td>-104.1</td>
<td>18.6</td>
</tr>
<tr>
<td>0.8</td>
<td>-7.2</td>
<td>-5.7</td>
</tr>
<tr>
<td>1.4</td>
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<td>-8.4</td>
</tr>
<tr>
<td>2.0</td>
<td>-14.1</td>
<td>-8.8</td>
</tr>
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<td></td>
</tr>
<tr>
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<tr>
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<td>-53.9</td>
</tr>
</tbody>
</table>

\[
\text{Error} = \frac{\sum (E_i^x - E_i^{\text{ref}})}{n}
\]
The Effective Fragment Molecular Orbital Method

Binding Energy per Water Molecule (kcal/mol)

<table>
<thead>
<tr>
<th>$R_{cut}$</th>
<th>FMO2</th>
<th>FIEFMO</th>
<th>MP2</th>
<th>FMO2</th>
<th>FIEFMO</th>
<th>MP2</th>
</tr>
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<tbody>
<tr>
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<td></td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>0.6</td>
<td>-23.7</td>
<td>-8.4</td>
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<td>-10.7</td>
<td>-10.3</td>
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<td>-9.3</td>
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<td>-11.7</td>
<td>-10.7</td>
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<td>-9.3</td>
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<td>32 water molecules</td>
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<td>-12.5</td>
<td>-10.8</td>
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<td>-11.3</td>
<td>-9.3</td>
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</tbody>
</table>
Energy contributions of each intermolecular interaction for all dimer interactions in a cluster of 8 water molecules and 2 benzene molecules.
The Effective Fragment Molecular Orbital Method

Timings performed on 10 nodes containing six 2.67 GHz Xeon X5650 cores per node with 24 GB of RAM

<table>
<thead>
<tr>
<th>R_cut</th>
<th>wall time</th>
<th>error</th>
<th>wall time</th>
<th>error</th>
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<td>6391</td>
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</table>

8 Water Molecules + 2 Benzene Molecules

<table>
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<tr>
<th>R_cut</th>
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<td>224</td>
<td>-40.2</td>
<td>2268</td>
<td>-22.1</td>
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</table>

8 Water Molecules + 8 Methanol Molecules

Times are in seconds, and errors are in kcal/mol
The Fragment Molecular Orbital Method

Important GAMESS modules

$FMO$

$GDDI$: Specifies parallel run

$FMOPRP$: Sets up convergers, properties

$FMOXYZ$: Similar to $DATA$

$FMOBND$: Bond detachment description

$OPTFMO$: Geometry optimization driver

$FMOHYB (FMOLMO)$: Fragmentation
The Fragment Molecular Orbital Method

Example Input
SCTRL SCIFYP=RHF RUNTP=OPTIMIZE MPEVL=2 NPRINT=9 $SEND
SCTRL ISFHER=1 SEND
$SYSTEM MMORDS=50 MMODI=8000 $SEND
$8BASIS BASIS=GRASSI NGAUSS=6 NDFUNC=1 NPRINT=1 $SEND
$8BASIS DIFFS=-T. DIFFSP=-T. $SEND
$SGDI NGROUP=4 $SEND
$SCF DIREC=-T. $SEND
$STATPT NSTEP=10000 $SEND
$END
NFRAG=4 NBODY=2
MPEVL(1)=2
INDAT(3)= 0, 1, -12,
           0, 12, -18,
           0, 19, -29,
           0, 30, -36,
           0
ICHARGP=1, -1, 1, -1
RESPAP=0 RESSPAP=-1 RESDIM=4 RCOND=4 $SEND
$SFMDPROP NPRINT=9 $SEND
$SFMTA
C1
H 1
C 6
N 7
O 8
$SEND
$SFMOXYZ
N  7  -1.6436481742  6.5598603693  4.0540010799
N  7   .6017808482  5.7521648546  4.380412608
C  6  -.8929974200  4.8890111712  5.3232025052
N  7  -2.1613985143  5.1484280856  5.6091019278
C  6  -.6822957882  6.1648675360  4.8778580648
H  1  .2831062363  5.7552108350  3.7923587454
```
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$SYSTEM MMORDS=25 MEMDII=400 $END
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$END
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$SMDRPP NPRINT=0 $END
$DATA
Cl
H 1
O 8
$END
$SMOXYZ
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</tr>
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```
C1
H 1
O 8

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</tr>
</tbody>
</table>
$fmo$

nbody=2
scfftyp(1)=rhf
modgrd=16 scffrg(1)=rhf,rhf,rhf,rhf,rhf
mult(1)=1,1,1,1,1
nfrwg-5 nlayer=1
icharg(1)= 0, 0, 0, 0, 0
frgnam(1)= alo002, alo002, phe003, alo004, alo005
indat(1)= 0

1  -6
  7  -10  13  -16  0
 11  12  17  -20  23  -26  0
 21  22  27  -30  33  -46  0
 31  32  47  -50  53  -56  0
 51  52  57  -60  63  -66  0
 61  62  67  -72  0

$end
$data
alpha /ACE-ALA/-ALA/-PHE/-ALA/-ALA-NME/
cl
h-1 1 1 0 0
c-1 6 2 0 0
n-1 7 3 0 0
o-1 8 4 0 0
$end
$$\text{$\text{SPINLD}$}
6-31G*  15 5
1 0  -0.065034  0.288264  0.000000  0.000000  0.000000  0.004413
  -0.017196  0.057935  0.000000  0.000000  0.000000
0 1  -0.065041  0.288284  0.563833  0.000000  0.000000  -0.201457
   0.290147  0.300784  0.000000  -0.106342  0.049599
   -0.017186  -0.008771  0.000000  -0.027223  0.000000
0 1  -0.065040  0.288293  -0.284927  -0.493490  -0.201456
   0.290146  -0.150393  -0.210487  -0.106341  -0.000428
   0.032923  -0.008771  0.033353  0.013612  0.023577
0 1  -0.065040  0.288293  -0.284917  0.493490  -0.201456
   0.290146  -0.150393  0.268487  -0.106341  -0.000428
   0.032923  -0.008771  -0.033353  0.013612  -0.023577
0 1  1.001938  -0.011976  0.000000  0.000000  0.000000
   -0.054085  0.000000  0.000000  -0.000001  -0.003175
   -0.003175  -0.003175  0.000000  0.000000  0.000000
$\text{MINI}$
5 5
1 0  -0.104883  0.308874  0.000000  0.000000  0.521806
0 1  -0.104883  0.308874  0.491961  0.000000  -0.173934
0 1  -0.104883  0.308876  -0.245980  -0.426050  -0.173933
0 1  -0.104883  0.308876  -0.245980  0.426050  -0.173933
0 1  0.988209  0.639929  0.000000  0.000000  0.000000
$$\text{$\text{SPINEND}$}
-9 11 6-31G* MINI
-19 21 6-31G* MINI
-29 31 6-31G* MINI
-49 51 6-31G* MINI
$$\text{$\text{SPINEND}$}
1 H  0.19300000  0.04100000  0.10200000
2 C  -0.41100000  0.35999999  -0.43580000
3 H  0.14399999  1.65600002  -0.63499999