# Tutorial on the ONIOM method for inorganic chemistry

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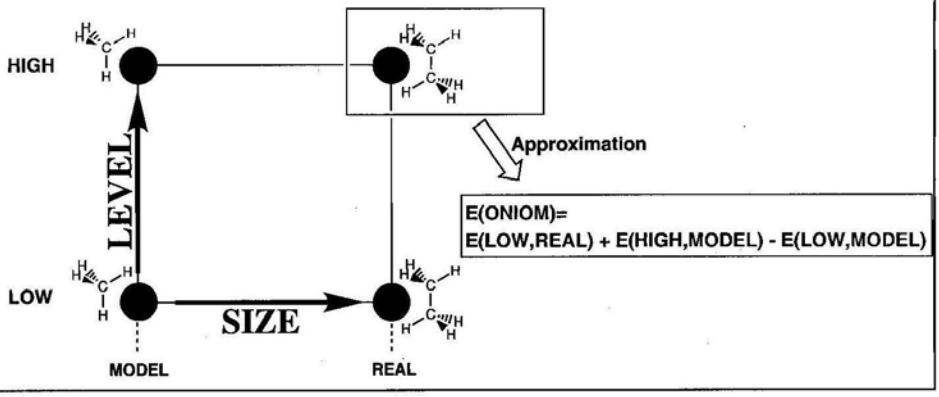
## 2-layer ONIOM

$\Delta E(HIGH,REAL) \approx \Delta E(ONIOM)$

E(ONIOM) = E(LOW;MODEL) + $\overrightarrow{SIZE}$ + $\overrightarrow{LEVEL}$

= E(LOW,MODEL) + [ E(LOW,REAL) - E(LOW,MODEL) ] + [ E(HIGH,MODEL) - E(LOW,MODEL) ]



## ONIOM2 Potential Energy Surface

**ONIOM energy**

**E(ONIOM) = E(LOW,REAL) + E(HIGH,MODEL) - E(LOW,MODEL)**

Potential energy surface well defined, and also derivatives are available.

**ONIOM gradient**

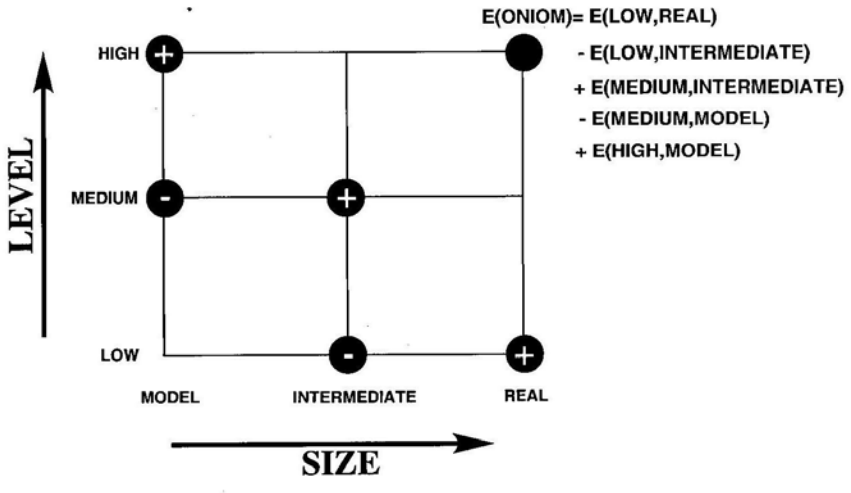
**G(ONIOM) = G(LOW,REAL) + G(HIGH,MODEL) x J - G(LOW,MODEL) x J**

J is the Jacobian that projects the forces off the link atoms onto the link atom hosts, and is a function of the atomic coordinates of the model system and link atom hosts.

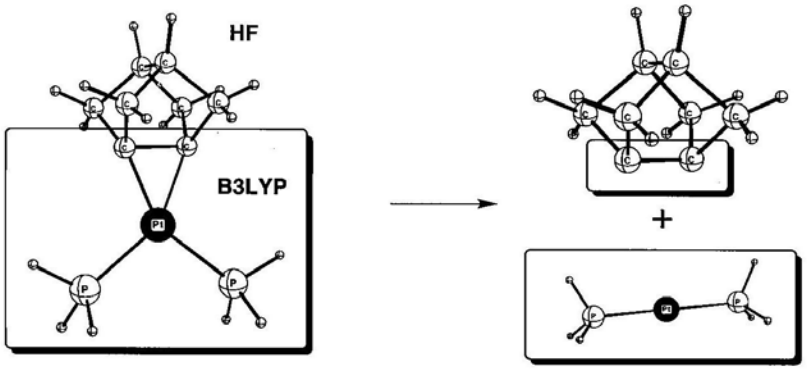
**ONIOM Hessian**

**H(ONIOM) = H(LOW,REAL) + $J^T$ x H(HIGH,MODEL) x J - $J^T$ x H(LOW,MODEL) x J**

## (3-layer) ONIOM3



## Example



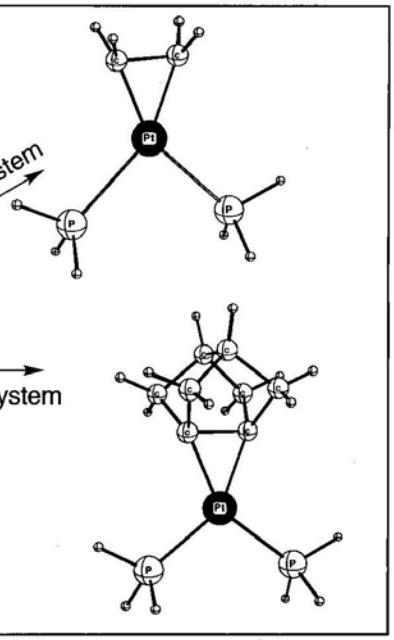

| | ΔE | Relative timing |
|---|---|---|
| HF | 86.6 kcal/mol | 0.08 |
| B3LYP | 53.6 | 1.00 |
| B3LYP:HF | 62.7 | 0.24 |

## Input

```
#P ONIOM(B3LYP/LANL2DZ:HF/LANL2MB)

Complex optimization B3LYP:HF

0 1
Pt    0.000    0.000    0.675
P     0.000    1.921    2.150
H     0.000    3.200    1.510
H     1.078    2.161    3.073
H    -1.078    2.161    3.073
P     0.000   -1.921    2.150
H     0.000   -3.200    1.510
H     1.078   -2.161    3.073
H    -1.078   -2.161    3.075
C     0.000    0.799   -1.240
C     0.000   -0.799   -1.240
C     1.169    1.165   -2.222 Low H
C    -1.169    1.165   -2.222 Low H
C     1.169   -1.165   -2.222 Low H
C    -1.169   -1.165   -2.222 Low H
C    -0.803    0.000   -3.188 Low
C     0.803    0.000   -3.188 Low
H    -1.264    0.000   -4.175 Low
H     1.264    0.000   -4.175 Low
H    -2.174    1.062   -1.827 Low
H    -1.062    2.161   -2.641 Low
H    -2.174   -1.062   -1.827 Low
```



## Output

```
-----------------------------
Complex optimized B3LYP:HF
-----------------------------
Symbolic Z-matrix:
Charge =  0 Multiplicity = 1
Charge =  0 Multiplicity = 1 in low level.
Pt                    0.        0.        0.675
P                     0.        1.921     2.15

ONIOM: Cut between C /H     12 and C     10 factor=  0.723886
ONIOM: Cut between C /H     13 and C     10 factor=  0.723886
ONIOM: Cut between C /H     14 and C     11 factor=  0.723886
ONIOM: Cut between C /H     15 and C     11 factor=  0.723886
ONIOM: generating new system at layer 2

SCF Done:  E(RHF) =  -439.188713773     A.U. after    8 cycles
           Convg  =    0.3541D-08             -V/T =  2.2594
           S**2   =    0.0000

SCF Done:  E(RB+HF-LYP) =  -214.273985270     A.U. after    8 cycles
           Convg  =    0.7972D-08             -V/T =  2.7308
           S**2   =    0.0000

SCF Done:  E(RHF) =  -211.180136595     A.U. after    8 cycles
           Convg  =    0.4163D-08             -V/T =  2.7206
           S**2   =    0.0000

ONIOM: extrapolated energy =    -442.282562448061
```

→ Charge and multiplicity

→ Link atoms

→ Real, low

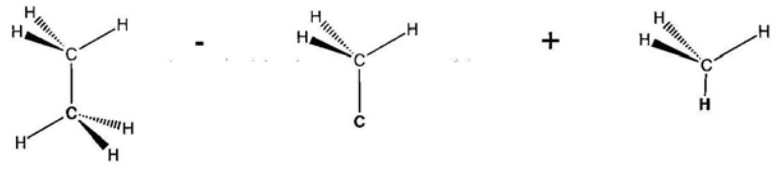
→ Model, high

→ Model, low

## IMOMM *(Maseras, Morokuma JCC, 16, p.1170, 1995)*

**Alternative link atom scheme**

**MM real system** - **MM model system** + **MO model system**



**E(IMOMM) = E(modelMO) + E(MM,real) - E(MM,modelMM)**

**= E(modelMO) + E(MM,real-only) + E(MM,interaction)**

**E(MM,interaction) consists of the MM terms that have centers in both layers**

## Bond-breaking energy in $C_{60}$

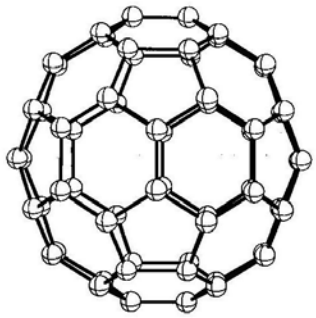
**(R.D.J. Froese, K. Morokuma, Chem. Phys. Letters, 305, 1999, 419)**

3-layer ONIOM, variety of method combinations investigated

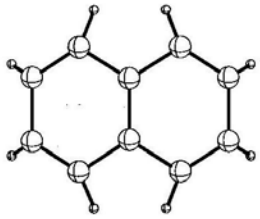
Geometries determined on AM1 level

Quintet corresponds to completely breaking the C=C bond

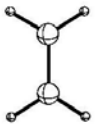
Triplet corresponds to breaking C=C $\pi$ bond



**Real System**



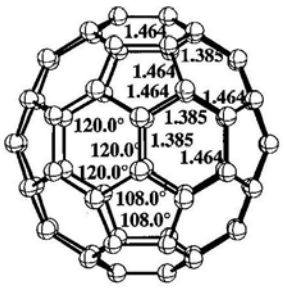
**Intermediate Model System**



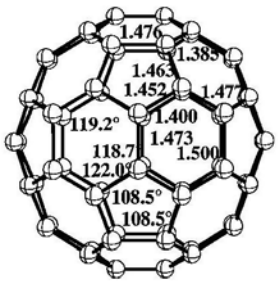
**Small Model System**

## Geometries of $C_{60}$ on AM1 level

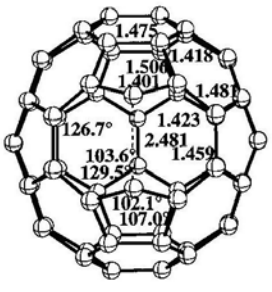
**These geometries have subsequently been used for the ONIOM3 calculations**




**Singlet**




**Triplet**

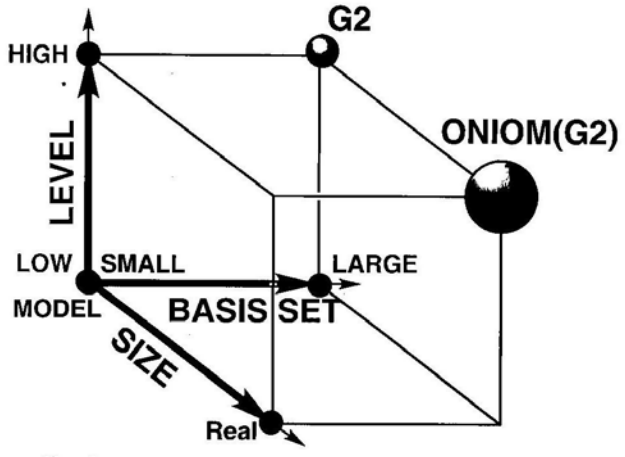



**Quintet**

## Singlet-Triplet and Singlet-Quintet Energy Separations

| | $S_0 \rightarrow T_1$ | $S_0 \rightarrow Q_1$ | | $S_0 \rightarrow T_1$ | $S_0 \rightarrow Q_1$ |
|---|---|---|---|---|---|
| *Real System* | | | *Correction Terms* | | |
| ROHF/6-31G | **48.4** (2.00) | 214.8 (6.00) | ΔE(ROHF/6-31G,real←int) | **-41.5** | 29.1 |
| UHF/6-31G | -47.5 (7.40) | 198.5 (6.69) | ΔE(UHF/6-31G,real←int) | -117.4 | 54.2 |
| | | | ΔE(ROHF,int←model) | 51.2 | 59.0 |
| *Intermediate Model System* | | | ΔE(UHF,int←model) | 34.1 | 45.8 |
| ROHF/6-31G(d) | 89.6 (2.00) | 185.8 (6.00) | ΔE(ROMP2,int←model) | **4.6** | 35.7 |
| UHF/6-31G(d) | 69.0 (2.38) | 167.2 (6.39) | ΔE(UMP2,int←model) | 27.1 | 54.1 |
| ROMP2/6-31G(d) | **73.4** | 217.4 | | | |
| UMP2/6-31G(d) | 95.8 | 235.2 | *Integrated Energies* | | |
| | | | E(G2MS(R):ROHF/6-31G:ROHF/6-31G) | 82.3 | 280.4 |
| *Small Model System* | | | E(G2MS(R):UHF/6-31G:UHF/6-31G) | -11.4 | 268.7 |
| ROHF/6-31G(d) | 38.4 (2.00) | 126.8 (6.00) | E(G2MS(R):ROMP2:UHF/6-31G) | -40.8 | 277.2 |
| UHF/6-31G(d) | 34.9 (2.01) | 121.4 (6.03) | E(G2MS(R):UMP2:ROHF/6-31G) | 57.6 | 270.5 |
| ROMP2/6-31G(d) | 68.8 | 181.7 | E(G2MS(R):ROMP2:ROHF/6-31G) | **35.1** | 252.1 |
| UMP2/6-31G(d) | 68.7 | 181.1 | E(G2MS(U):ROMP2:ROHF/6-31G) | **35.5** | 252.8 |
| ROMP2/6-311+G(2df,2p) | 71.6 | 187.8 | | | |
| UMP2/6-311+G(2df,2p) | 71.8 | 187.9 | *Experimental* | **36.1** | |
| UMP4SDQ/6-31G(d) | 66.0 | 177.1 | | | |
| UCCSD(T)/6-31G(d) | 69.3 | 181.2 | | | |
| G2MS(ROMP2) | **72.0** | 187.3 | | | |
| G2MS(UMP2) | **72.4** | 188.0 | | | |

## G2 methods in combination with ONIOM: Integration in three dimensions




**Our G2-like method:**

E[G2MS(R)] = E[CCSD(T)/6-31G(d)] + E[ROMP2/6-311+G(2df,2p)] – E[ROMP2/6-31G(d)]

E[G2MS(U)] = E[CCSD(T)/6-31G(d)] + E[UMP2/6-311+G(2df,2p)] – E[UMP2/6-31G(d)]

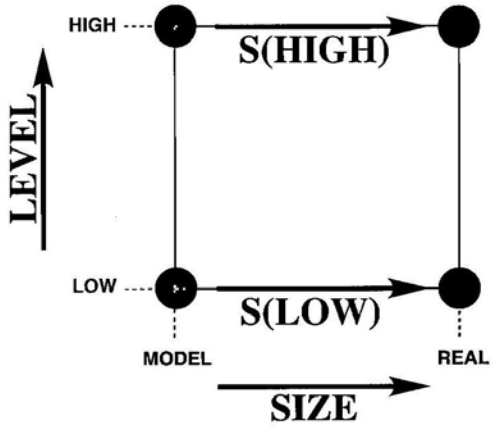
## S(ubstituent)-Value test: Testing ONIOM

**Choice of combination of levels is critical**

**Combinations can be investigated using the S-Value test**

**S(LEVEL) = E(LEVEL,REAL) - E(LEVEL,MODEL)**

**Several E(HIGH,REAL) calculations necessary**




**S(HIGH) = S(LOW)**

⇩

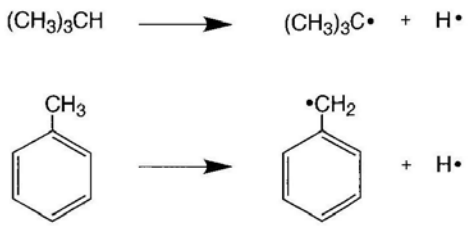
**E(ONIOM) = E(HIGH,REAL)**

**S(HIGH) - S(LOW)**

⇩

**Must be as close to zero as possible**

## S-Value test: example




| level | *iso*-butane | toluene |
|---|---|---|
| **G2MS(R)** | -7.75(0.00) | -16.21(0.00) |
| **UHF** | -7.29(+0.46) | -26.12(-9.91) |
| **RHF** | -6.73(+1.02) | -10.28(+5.93) |
| **UMP2** | -7.72(+0.03) | +6.93(+23.14) |
| **RMP2** | -8.10(-0.35) | -15.04(+1.17) |

## ONIOM(MO:MM)

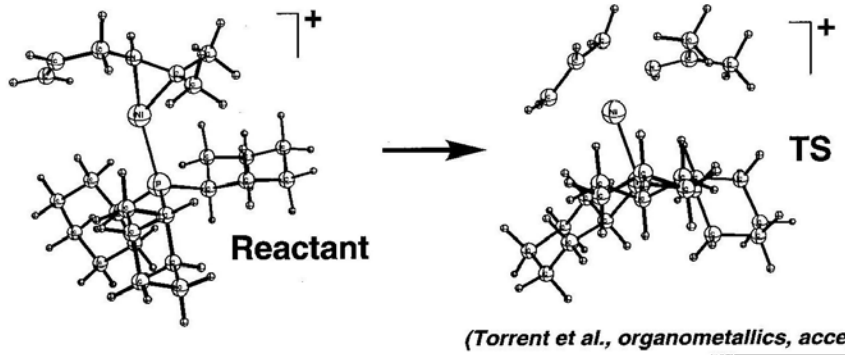
**Pure Molecular Mechanics:**

**MM terms must be the same for species that are to be compared**
**(Atom types and connectivity changes upon dissociation)**

**⟶ Bond breaking/forming can not be studied**

**ONIOM(MO:MM) ⟶ Bond breaking/forming in MO region**

**Changing terms must cancel from energy expression**

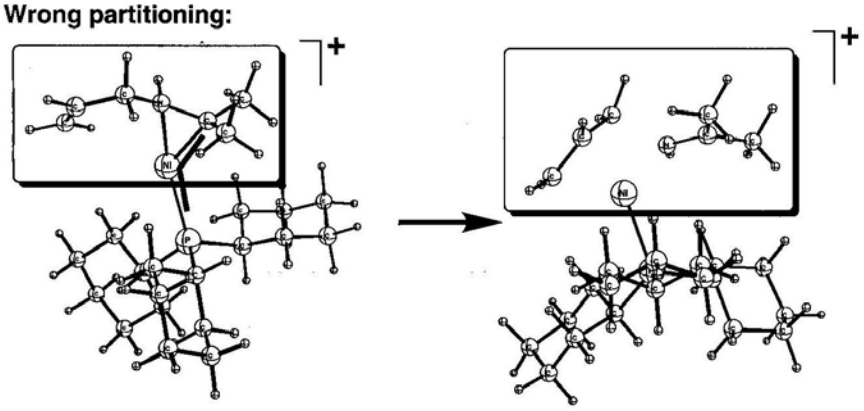



***(Torrent et al., organometallics, accepted)***

## ONIOM(MO:MM)

**"Results must be independent on definition of bonds in reaction center"**

**Wrong partitioning:**



**Indicated angular term (and others) is different in model and real system**

**Model: C-Ni-H  Real: C-Ni-P**

**⟶ Result depends on whether C-Ni is defined as bond or not**

# ONIOM(MO:MM)

**How to recognize improper cancellation in ONIOM(MO:MM)?**

**Safe:**

**Bond breaking/forming processes at least three bonds from MM region**

**⟶ Might end up with unnecessarily expensive model system**

**Easy:**

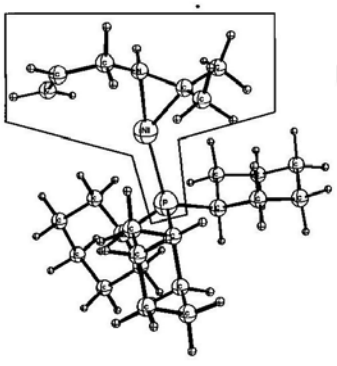
**Calculate E(MM,real) - E(MM,model) = S(MM) for alternative connectivities**

**S-values for reactant at UFF level (Hartrees):**

| | Bonds as in reactant | | | Bonds as in TS | | |
|---|---|---|---|---|---|---|
| | Model | Real | S-value | Model | Real | S-value |
| Stretch | 0.00674 | 0.01197 | 0.00523 | 0.00349 | 0.00873 | 0.00523 |
| Bend | 0.47259 | 0.68288 | 0.21029 | 0.03970 | 0.10388 | 0.06418 |
| Torsion | 0.0029 | 0.00681 | 0.00381 | 0.00278 | 0.00659 | 0.00381 |
| Improper torsion | 0.00000 | 0.00000 | 0.00000 | 0.00000 | 0.00000 | 0.00000 |
| Vanderwaals | 0.00618 | 0.01213 | 0.00595 | 0.06560 | 0.07128 | 0.00568 |
| Total | 0.48849 | 0.71378 | 0.22529 | 0.11158 | 0.19048 | 0.07891 |

# ONIOM(MO:MM)

**Correct partitioning**



| | Bonds as in reactant | | |
|---|---|---|---|
| | Model | Real | S-value |
| Stretch | 0.00700 | 0.01197 | 0.00497 |
| Bend | 0.64118 | 0.68288 | 0.04170 |
| Torsion | 0.00299 | 0.00681 | 0.00381 |
| Improper torsion | 0.00000 | 0.00000 | 0.00000 |
| Vanderwaals | 0.00455 | 0.01213 | 0.00758 |
| Total | 0.65572 | 0.71378 | 0.05806 |

| | Bonds as in TS | | |
|---|---|---|---|
| | Model | Real | S-value |
| Stretch | 0.00376 | 0.00873 | 0.00497 |
| Bend | 0.06218 | 0.10388 | 0.04170 |
| Torsion | 0.00278 | 0.00659 | 0.00381 |
| Improper torsion | 0.00000 | 0.00000 | 0.00000 |
| Vanderwaals | 0.06371 | 0.07128 | 0.00758 |
| Total | 0.13242 | 0.19048 | 0.05806 |

*ONIOM Development and Applications*

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