Supporting Information
Incremental Embedding: A Density Matrix Embedding Scheme for Molecules

Hong-Zhou Ye[1], Matthew Welborn[1,2], Nathan D. Ricke[1], and Troy Van Voorhis*[1]

[1] *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, 02139*
[2] *Current address: Department of Chemistry, California Institute of Technology, Pasadena, CA 91125*

Note: figures and tables in the main text are referred as Figure Mxxx and Table Mxxx.

1 Molecular structures

Shown below are the geometries (xyz format) used in the calculation in the main text. The equilibrium structures are obtained by geometry optimization at B3LYP/cc-pVTZ level in Q-Chem[1].

- H_{10} (radial expansion):

```
10
0.50
H 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 0.5000000000
H 0.2938926261 0.0000000000 0.9045084972
H 0.7694208843 0.0000000000 1.0590169944
H 1.2449491424 0.0000000000 0.9045084972
H 1.5388417686 0.0000000000 0.5000000000
H 1.5388417686 0.0000000000 -0.0000000000
H 1.2449491424 0.0000000000 -0.4045084972
H 0.7694208843 0.0000000000 -0.5590169944
H 0.2938926261 0.0000000000 -0.4045084972

10
0.55
H 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 0.5500000000
H 0.3232818888 0.0000000000 0.9949593469
H 0.8463629727 0.0000000000 1.1649186938
H 1.3694440567 0.0000000000 0.9949593469
H 1.6927259454 0.0000000000 0.5500000000
H 1.6927259454 0.0000000000 -0.0000000000
H 1.3694440567 0.0000000000 -0.4449593469
H 0.8463629727 0.0000000000 -0.6149186938
H 0.3232818888 0.0000000000 -0.4449593469

10
0.60
H 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 0.6000000000
H 0.3526711514 0.0000000000 1.0854101966
```

*tvan@mit.edu

[1] Shao, Y. *et. al. Mol. Phys.* **2015**, 113, 184–215.

```
H 0.9233050612 0.0000000000 1.2708203932
H 1.4939389709 0.0000000000 1.0854101966
H 1.8466101223 0.0000000000 0.6000000000
H 1.8466101223 0.0000000000 -0.0000000000
H 1.4939389709 0.0000000000 -0.4854101966
H 0.9233050612 0.0000000000 -0.6708203932
H 0.3526711514 0.0000000000 -0.4854101966

10
0.65
H 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 0.6500000000
H 0.3820604140 0.0000000000 1.1758610463
H 1.0002471496 0.0000000000 1.3767220927
H 1.6184338852 0.0000000000 1.1758610463
H 2.0004942992 0.0000000000 0.6500000000
H 2.0004942992 0.0000000000 -0.0000000000
H 1.6184338852 0.0000000000 -0.5258610463
H 1.0002471496 0.0000000000 -0.7267220927
H 0.3820604140 0.0000000000 -0.5258610463

10
0.70
H 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 0.7000000000
H 0.4114496766 0.0000000000 1.2663118961
H 1.0771892380 0.0000000000 1.4826237921
H 1.7429287994 0.0000000000 1.2663118961
H 2.1543784760 0.0000000000 0.7000000000
H 2.1543784760 0.0000000000 -0.0000000000
H 1.7429287994 0.0000000000 -0.5663118961
H 1.0771892380 0.0000000000 -0.7826237921
H 0.4114496766 0.0000000000 -0.5663118961

10
0.75
H 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 0.7500000000
H 0.4408389392 0.0000000000 1.3567627458
H 1.1541313264 0.0000000000 1.5885254916
H 1.8674237137 0.0000000000 1.3567627458
H 2.3082626529 0.0000000000 0.7500000000
H 2.3082626529 0.0000000000 -0.0000000000
H 1.8674237137 0.0000000000 -0.6067627458
H 1.1541313264 0.0000000000 -0.8385254916
H 0.4408389392 0.0000000000 -0.6067627458

10
0.80
H 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 0.8000000000
H 0.4702282018 0.0000000000 1.4472135955
H 1.2310734149 0.0000000000 1.6944271910
H 1.9919186279 0.0000000000 1.4472135955
H 2.4621468297 0.0000000000 0.8000000000
H 2.4621468297 0.0000000000 -0.0000000000
H 1.9919186279 0.0000000000 -0.6472135955
H 1.2310734149 0.0000000000 -0.8944271910
```

```
H 0.4702282018 0.0000000000 -0.6472135955

10
0.85
H 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 0.8500000000
H 0.4996174644 0.0000000000 1.5376644452
H 1.3080155033 0.0000000000 1.8003288904
H 2.1164135422 0.0000000000 1.5376644452
H 2.6160310066 0.0000000000 0.8500000000
H 2.6160310066 0.0000000000 -0.0000000000
H 2.1164135422 0.0000000000 -0.6876644452
H 1.3080155033 0.0000000000 -0.9503288904
H 0.4996174644 0.0000000000 -0.6876644452

10
0.90
H 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 0.9000000000
H 0.5290067271 0.0000000000 1.6281152949
H 1.3849575917 0.0000000000 1.9062305899
H 2.2409084564 0.0000000000 1.6281152949
H 2.7699151835 0.0000000000 0.9000000000
H 2.7699151835 0.0000000000 -0.0000000000
H 2.2409084564 0.0000000000 -0.7281152949
H 1.3849575917 0.0000000000 -1.0062305899
H 0.5290067271 0.0000000000 -0.7281152949

10
0.95
H 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 0.9500000000
H 0.5583959897 0.0000000000 1.7185661447
H 1.4618996802 0.0000000000 2.0121322893
H 2.3654033706 0.0000000000 1.7185661447
H 2.9237993603 0.0000000000 0.9500000000
H 2.9237993603 0.0000000000 -0.0000000000
H 2.3654033706 0.0000000000 -0.7685661447
H 1.4618996802 0.0000000000 -1.0621322893
H 0.5583959897 0.0000000000 -0.7685661447

10
1.00
H 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0000000000
H 0.5877852523 0.0000000000 1.8090169944
H 1.5388417686 0.0000000000 2.1180339887
H 2.4898982849 0.0000000000 1.8090169944
H 3.0776835372 0.0000000000 1.0000000000
H 3.0776835372 0.0000000000 -0.0000000000
H 2.4898982849 0.0000000000 -0.8090169944
H 1.5388417686 0.0000000000 -1.1180339887
H 0.5877852523 0.0000000000 -0.8090169944

10
1.05
H 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0500000000
```

```
H 0.6171745149 0.0000000000 1.8994678441
H 1.6157838570 0.0000000000 2.2239356882
H 2.6143931991 0.0000000000 1.8994678441
H 3.2315677140 0.0000000000 1.0500000000
H 3.2315677140 0.0000000000 -0.0000000000
H 2.6143931991 0.0000000000 -0.8494678441
H 1.6157838570 0.0000000000 -1.1739356882
H 0.6171745149 0.0000000000 -0.8494678441

10
1.10
H 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.1000000000
H 0.6465637775 0.0000000000 1.9899186938
H 1.6927259454 0.0000000000 2.3298373876
H 2.7388881134 0.0000000000 1.9899186938
H 3.3854518909 0.0000000000 1.1000000000
H 3.3854518909 0.0000000000 -0.0000000000
H 2.7388881134 0.0000000000 -0.8899186938
H 1.6927259454 0.0000000000 -1.2298373876
H 0.6465637775 0.0000000000 -0.8899186938

10
1.15
H 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.1500000000
H 0.6759530401 0.0000000000 2.0803695435
H 1.7696680339 0.0000000000 2.4357390871
H 2.8633830276 0.0000000000 2.0803695435
H 3.5393360678 0.0000000000 1.1500000000
H 3.5393360678 0.0000000000 -0.0000000000
H 2.8633830276 0.0000000000 -0.9303695435
H 1.7696680339 0.0000000000 -1.2857390871
H 0.6759530401 0.0000000000 -0.9303695435

10
1.20
H 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.2000000000
H 0.7053423028 0.0000000000 2.1708203932
H 1.8466101223 0.0000000000 2.5416407865
H 2.9878779419 0.0000000000 2.1708203932
H 3.6932202446 0.0000000000 1.2000000000
H 3.6932202446 0.0000000000 -0.0000000000
H 2.9878779419 0.0000000000 -0.9708203932
H 1.8466101223 0.0000000000 -1.3416407865
H 0.7053423028 0.0000000000 -0.9708203932

10
1.25
H 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.2500000000
H 0.7347315654 0.0000000000 2.2612712430
H 1.9235522107 0.0000000000 2.6475424859
H 3.1123728561 0.0000000000 2.2612712430
H 3.8471044215 0.0000000000 1.2500000000
H 3.8471044215 0.0000000000 -0.0000000000
H 3.1123728561 0.0000000000 -1.0112712430
```

```
H 1.9235522107 0.0000000000 -1.3975424859
H 0.7347315654 0.0000000000 -1.0112712430

10
1.30
H 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.3000000000
H 0.7641208280 0.0000000000 2.3517220927
H 2.0004942992 0.0000000000 2.7534441854
H 3.2368677703 0.0000000000 2.3517220927
H 4.0009885983 0.0000000000 1.3000000000
H 4.0009885983 0.0000000000 -0.0000000000
H 3.2368677703 0.0000000000 -1.0517220927
H 2.0004942992 0.0000000000 -1.4534441854
H 0.7641208280 0.0000000000 -1.0517220927

10
1.35
H 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.3500000000
H 0.7935100906 0.0000000000 2.4421729424
H 2.0774363876 0.0000000000 2.8593458848
H 3.3613626846 0.0000000000 2.4421729424
H 4.1548727752 0.0000000000 1.3500000000
H 4.1548727752 0.0000000000 -0.0000000000
H 3.3613626846 0.0000000000 -1.0921729424
H 2.0774363876 0.0000000000 -1.5093458848
H 0.7935100906 0.0000000000 -1.0921729424

10
1.40
H 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.4000000000
H 0.8228993532 0.0000000000 2.5326237921
H 2.1543784760 0.0000000000 2.9652475842
H 3.4858575988 0.0000000000 2.5326237921
H 4.3087569520 0.0000000000 1.4000000000
H 4.3087569520 0.0000000000 -0.0000000000
H 3.4858575988 0.0000000000 -1.1326237921
H 2.1543784760 0.0000000000 -1.5652475842
H 0.8228993532 0.0000000000 -1.1326237921

10
1.45
H 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.4500000000
H 0.8522886158 0.0000000000 2.6230746418
H 2.2313205645 0.0000000000 3.0711492837
H 3.6103525131 0.0000000000 2.6230746418
H 4.4626411289 0.0000000000 1.4500000000
H 4.4626411289 0.0000000000 -0.0000000000
H 3.6103525131 0.0000000000 -1.1730746418
H 2.2313205645 0.0000000000 -1.6211492837
H 0.8522886158 0.0000000000 -1.1730746418

10
1.50
H 0.0000000000 0.0000000000 0.0000000000
```

```
H 0.0000000000 0.0000000000 1.5000000000
H 0.8816778784 0.0000000000 2.7135254916
H 2.3082626529 0.0000000000 3.1770509831
H 3.7348474273 0.0000000000 2.7135254916
H 4.6165253058 0.0000000000 1.5000000000
H 4.6165253058 0.0000000000 -0.0000000000
H 3.7348474273 0.0000000000 -1.2135254916
H 2.3082626529 0.0000000000 -1.6770509831
H 0.8816778784 0.0000000000 -1.2135254916

10
1.60
H 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.6000000000
H 0.9404564037 0.0000000000 2.8944271910
H 2.4621468297 0.0000000000 3.3888543820
H 3.9838372558 0.0000000000 2.8944271910
H 4.9242936595 0.0000000000 1.6000000000
H 4.9242936595 0.0000000000 -0.0000000000
H 3.9838372558 0.0000000000 -1.2944271910
H 2.4621468297 0.0000000000 -1.7888543820
H 0.9404564037 0.0000000000 -1.2944271910

10
1.70
H 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.7000000000
H 0.9992349289 0.0000000000 3.0753288904
H 2.6160310066 0.0000000000 3.6006577809
H 4.2328270843 0.0000000000 3.0753288904
H 5.2320620132 0.0000000000 1.7000000000
H 5.2320620132 0.0000000000 -0.0000000000
H 4.2328270843 0.0000000000 -1.3753288904
H 2.6160310066 0.0000000000 -1.9006577809
H 0.9992349289 0.0000000000 -1.3753288904

10
1.80
H 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.8000000000
H 1.0580134541 0.0000000000 3.2562305899
H 2.7699151835 0.0000000000 3.8124611797
H 4.4818169128 0.0000000000 3.2562305899
H 5.5398303669 0.0000000000 1.8000000000
H 5.5398303669 0.0000000000 -0.0000000000
H 4.4818169128 0.0000000000 -1.4562305899
H 2.7699151835 0.0000000000 -2.0124611797
H 1.0580134541 0.0000000000 -1.4562305899

10
1.90
H 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.9000000000
H 1.1167919794 0.0000000000 3.4371322893
H 2.9237993603 0.0000000000 4.0242645786
H 4.7308067413 0.0000000000 3.4371322893
H 5.8475987206 0.0000000000 1.9000000000
H 5.8475987206 0.0000000000 -0.0000000000
```

```
H 4.7308067413 0.0000000000 -1.5371322893
H 2.9237993603 0.0000000000 -2.1242645786
H 1.1167919794 0.0000000000 -1.5371322893

10
2.00
H 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 2.0000000000
H 1.1755705046 0.0000000000 3.6180339887
H 3.0776835372 0.0000000000 4.2360679775
H 4.9797965698 0.0000000000 3.6180339887
H 6.1553670744 0.0000000000 2.0000000000
H 6.1553670744 0.0000000000 -0.0000000000
H 4.9797965698 0.0000000000 -1.6180339887
H 3.0776835372 0.0000000000 -2.2360679775
H 1.1755705046 0.0000000000 -1.6180339887

10
2.10
H 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 2.1000000000
H 1.2343490298 0.0000000000 3.7989356882
H 3.2315677140 0.0000000000 4.4478713764
H 5.2287863983 0.0000000000 3.7989356882
H 6.4631354281 0.0000000000 2.1000000000
H 6.4631354281 0.0000000000 -0.0000000000
H 5.2287863983 0.0000000000 -1.6989356882
H 3.2315677140 0.0000000000 -2.3478713764
H 1.2343490298 0.0000000000 -1.6989356882

10
2.20
H 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 2.2000000000
H 1.2931275550 0.0000000000 3.9798373876
H 3.3854518909 0.0000000000 4.6596747752
H 5.4777762267 0.0000000000 3.9798373876
H 6.7709037818 0.0000000000 2.2000000000
H 6.7709037818 0.0000000000 -0.0000000000
H 5.4777762267 0.0000000000 -1.7798373876
H 3.3854518909 0.0000000000 -2.4596747752
H 1.2931275550 0.0000000000 -1.7798373876

10
2.30
H 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 2.3000000000
H 1.3519060803 0.0000000000 4.1607390871
H 3.5393360678 0.0000000000 4.8714781741
H 5.7267660552 0.0000000000 4.1607390871
H 7.0786721355 0.0000000000 2.3000000000
H 7.0786721355 0.0000000000 -0.0000000000
H 5.7267660552 0.0000000000 -1.8607390871
H 3.5393360678 0.0000000000 -2.5714781741
H 1.3519060803 0.0000000000 -1.8607390871

10
2.40
```

```
H 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 2.4000000000
H 1.4106846055 0.0000000000 4.3416407865
H 3.6932202446 0.0000000000 5.0832815730
H 5.9757558837 0.0000000000 4.3416407865
H 7.3864404892 0.0000000000 2.4000000000
H 7.3864404892 0.0000000000 -0.0000000000
H 5.9757558837 0.0000000000 -1.9416407865
H 3.6932202446 0.0000000000 -2.6832815730
H 1.4106846055 0.0000000000 -1.9416407865

10
2.50
H 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 2.5000000000
H 1.4694631307 0.0000000000 4.5225424859
H 3.8471044215 0.0000000000 5.2950849719
H 6.2247457122 0.0000000000 4.5225424859
H 7.6942088429 0.0000000000 2.5000000000
H 7.6942088429 0.0000000000 -0.0000000000
H 6.2247457122 0.0000000000 -2.0225424859
H 3.8471044215 0.0000000000 -2.7950849719
H 1.4694631307 0.0000000000 -2.0225424859
```

- CH_4 (homolytic dissociation of one C–H bond):

```
5
0.70
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 0.7000000000
H 1.0260649157 0.0000000000 -0.3627801605
H -0.5130521462 -0.8885870764 -0.3627797665
H -0.5130261191 0.8886085072 -0.3627670806

5
0.75
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 0.7500000000
H 1.0260649157 0.0000000000 -0.3627801605
H -0.5130521462 -0.8885870764 -0.3627797665
H -0.5130261191 0.8886085072 -0.3627670806

5
0.80
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 0.8000000000
H 1.0260649157 0.0000000000 -0.3627801605
H -0.5130521462 -0.8885870764 -0.3627797665
H -0.5130261191 0.8886085072 -0.3627670806

5
0.85
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 0.8500000000
H 1.0260649157 0.0000000000 -0.3627801605
H -0.5130521462 -0.8885870764 -0.3627797665
H -0.5130261191 0.8886085072 -0.3627670806
```

```
5
0.90
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 0.9000000000
H 1.0260649157 0.0000000000 -0.3627801605
H -0.5130521462 -0.8885870764 -0.3627797665
H -0.5130261191 0.8886085072 -0.3627670806

5
0.95
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 0.9500000000
H 1.0260649157 0.0000000000 -0.3627801605
H -0.5130521462 -0.8885870764 -0.3627797665
H -0.5130261191 0.8886085072 -0.3627670806

5
1.00
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0000000000
H 1.0260649157 0.0000000000 -0.3627801605
H -0.5130521462 -0.8885870764 -0.3627797665
H -0.5130261191 0.8886085072 -0.3627670806

5
1.05
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0500000000
H 1.0260649157 0.0000000000 -0.3627801605
H -0.5130521462 -0.8885870764 -0.3627797665
H -0.5130261191 0.8886085072 -0.3627670806

5
1.10
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.1000000000
H 1.0260649157 0.0000000000 -0.3627801605
H -0.5130521462 -0.8885870764 -0.3627797665
H -0.5130261191 0.8886085072 -0.3627670806

5
1.15
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.1500000000
H 1.0260649157 0.0000000000 -0.3627801605
H -0.5130521462 -0.8885870764 -0.3627797665
H -0.5130261191 0.8886085072 -0.3627670806

5
1.20
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.2000000000
H 1.0260649157 0.0000000000 -0.3627801605
H -0.5130521462 -0.8885870764 -0.3627797665
H -0.5130261191 0.8886085072 -0.3627670806

5
1.25
```

```
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.2500000000
H 1.0260649157 0.0000000000 -0.3627801605
H -0.5130521462 -0.8885870764 -0.3627797665
H -0.5130261191 0.8886085072 -0.3627670806

5
1.30
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.3000000000
H 1.0260649157 0.0000000000 -0.3627801605
H -0.5130521462 -0.8885870764 -0.3627797665
H -0.5130261191 0.8886085072 -0.3627670806

5
1.35
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.3500000000
H 1.0260649157 0.0000000000 -0.3627801605
H -0.5130521462 -0.8885870764 -0.3627797665
H -0.5130261191 0.8886085072 -0.3627670806

5
1.40
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.4000000000
H 1.0260649157 0.0000000000 -0.3627801605
H -0.5130521462 -0.8885870764 -0.3627797665
H -0.5130261191 0.8886085072 -0.3627670806

5
1.45
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.4500000000
H 1.0260649157 0.0000000000 -0.3627801605
H -0.5130521462 -0.8885870764 -0.3627797665
H -0.5130261191 0.8886085072 -0.3627670806

5
1.50
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.5000000000
H 1.0260649157 0.0000000000 -0.3627801605
H -0.5130521462 -0.8885870764 -0.3627797665
H -0.5130261191 0.8886085072 -0.3627670806

5
1.55
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.5500000000
H 1.0260649157 0.0000000000 -0.3627801605
H -0.5130521462 -0.8885870764 -0.3627797665
H -0.5130261191 0.8886085072 -0.3627670806

5
1.60
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.6000000000
```

```
H 1.0260649157 0.0000000000 -0.3627801605
H -0.5130521462 -0.8885870764 -0.3627797665
H -0.5130261191 0.8886085072 -0.3627670806

5
1.65
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.6500000000
H 1.0260649157 0.0000000000 -0.3627801605
H -0.5130521462 -0.8885870764 -0.3627797665
H -0.5130261191 0.8886085072 -0.3627670806

5
1.70
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.7000000000
H 1.0260649157 0.0000000000 -0.3627801605
H -0.5130521462 -0.8885870764 -0.3627797665
H -0.5130261191 0.8886085072 -0.3627670806

5
1.75
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.7500000000
H 1.0260649157 0.0000000000 -0.3627801605
H -0.5130521462 -0.8885870764 -0.3627797665
H -0.5130261191 0.8886085072 -0.3627670806

5
1.80
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.8000000000
H 1.0260649157 0.0000000000 -0.3627801605
H -0.5130521462 -0.8885870764 -0.3627797665
H -0.5130261191 0.8886085072 -0.3627670806

5
1.85
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.8500000000
H 1.0260649157 0.0000000000 -0.3627801605
H -0.5130521462 -0.8885870764 -0.3627797665
H -0.5130261191 0.8886085072 -0.3627670806

5
1.90
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.9000000000
H 1.0260649157 0.0000000000 -0.3627801605
H -0.5130521462 -0.8885870764 -0.3627797665
H -0.5130261191 0.8886085072 -0.3627670806

5
1.95
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.9500000000
H 1.0260649157 0.0000000000 -0.3627801605
H -0.5130521462 -0.8885870764 -0.3627797665
```

```
H -0.5130261191 0.8886085072 -0.3627670806

5
2.00
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 2.0000000000
H 1.0260649157 0.0000000000 -0.3627801605
H -0.5130521462 -0.8885870764 -0.3627797665
H -0.5130261191 0.8886085072 -0.3627670806

5
2.10
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 2.1000000000
H 1.0260649157 0.0000000000 -0.3627801605
H -0.5130521462 -0.8885870764 -0.3627797665
H -0.5130261191 0.8886085072 -0.3627670806

5
2.20
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 2.2000000000
H 1.0260649157 0.0000000000 -0.3627801605
H -0.5130521462 -0.8885870764 -0.3627797665
H -0.5130261191 0.8886085072 -0.3627670806

5
2.30
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 2.3000000000
H 1.0260649157 0.0000000000 -0.3627801605
H -0.5130521462 -0.8885870764 -0.3627797665
H -0.5130261191 0.8886085072 -0.3627670806

5
2.40
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 2.4000000000
H 1.0260649157 0.0000000000 -0.3627801605
H -0.5130521462 -0.8885870764 -0.3627797665
H -0.5130261191 0.8886085072 -0.3627670806

5
2.50
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 2.5000000000
H 1.0260649157 0.0000000000 -0.3627801605
H -0.5130521462 -0.8885870764 -0.3627797665
H -0.5130261191 0.8886085072 -0.3627670806

5
2.60
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 2.6000000000
H 1.0260649157 0.0000000000 -0.3627801605
H -0.5130521462 -0.8885870764 -0.3627797665
H -0.5130261191 0.8886085072 -0.3627670806
```

```
5
2.70
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 2.7000000000
H 1.0260649157 0.0000000000 -0.3627801605
H -0.5130521462 -0.8885870764 -0.3627797665
H -0.5130261191 0.8886085072 -0.3627670806

5
2.80
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 2.8000000000
H 1.0260649157 0.0000000000 -0.3627801605
H -0.5130521462 -0.8885870764 -0.3627797665
H -0.5130261191 0.8886085072 -0.3627670806

5
2.90
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 2.9000000000
H 1.0260649157 0.0000000000 -0.3627801605
H -0.5130521462 -0.8885870764 -0.3627797665
H -0.5130261191 0.8886085072 -0.3627670806

5
3.00
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 3.0000000000
H 1.0260649157 0.0000000000 -0.3627801605
H -0.5130521462 -0.8885870764 -0.3627797665
H -0.5130261191 0.8886085072 -0.3627670806
```

- C_2H_6 (homolytic dissociation of the C−C bond):

```
8
1.00
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0910530000
H 1.0404571178 0.0000000000 -0.3284085581
H -0.4480430575 0.9390393681 -0.3284324300
C -0.4968924884 -0.7876776211 -0.3642277037
H -0.4968924884 -0.7876776211 -1.4552807037
H -1.5373497404 -0.7876773506 -0.0358195706
H -0.0488497180 -1.7267169799 -0.0357948553

8
1.05
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0910530000
H 1.0404571178 0.0000000000 -0.3284085581
H -0.4480430575 0.9390393681 -0.3284324300
C -0.5217371128 -0.8270615022 -0.3824390888
H -0.5217371128 -0.8270615022 -1.4734920888
H -1.5621943649 -0.8270612316 -0.0540309558
H -0.0736943424 -1.7661008609 -0.0540062405

8
1.10
```

```
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0910530000
H 1.0404571178 0.0000000000 -0.3284085581
H -0.4480430575 0.9390393681 -0.3284324300
C -0.5465817373 -0.8664453832 -0.4006504740
H -0.5465817373 -0.8664453832 -1.4917034740
H -1.5870389893 -0.8664451127 -0.0722423410
H -0.0985389668 -1.8054847420 -0.0722176257

8
1.15
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0910530000
H 1.0404571178 0.0000000000 -0.3284085581
H -0.4480430575 0.9390393681 -0.3284324300
C -0.5714263617 -0.9058292643 -0.4188618592
H -0.5714263617 -0.9058292643 -1.5099148592
H -1.6118836137 -0.9058289937 -0.0904537261
H -0.1233835913 -1.8448686230 -0.0904290109

8
1.20
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0910530000
H 1.0404571178 0.0000000000 -0.3284085581
H -0.4480430575 0.9390393681 -0.3284324300
C -0.5962709861 -0.9452131454 -0.4370732444
H -0.5962709861 -0.9452131454 -1.5281262444
H -1.6367282381 -0.9452128748 -0.1086651113
H -0.1482282157 -1.8842525041 -0.1086403960

8
1.25
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0910530000
H 1.0404571178 0.0000000000 -0.3284085581
H -0.4480430575 0.9390393681 -0.3284324300
C -0.6211156105 -0.9845970264 -0.4552846296
H -0.6211156105 -0.9845970264 -1.5463376296
H -1.6615728625 -0.9845967559 -0.1268764965
H -0.1730728401 -1.9236363851 -0.1268517812

8
1.30
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0910530000
H 1.0404571178 0.0000000000 -0.3284085581
H -0.4480430575 0.9390393681 -0.3284324300
C -0.6459602350 -1.0239809075 -0.4734960148
H -0.6459602350 -1.0239809075 -1.5645490148
H -1.6864174870 -1.0239806369 -0.1450878817
H -0.1979174645 -1.9630202662 -0.1450631664

8
1.35
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0910530000
H 1.0404571178 0.0000000000 -0.3284085581
```

```
H -0.4480430575 0.9390393681 -0.3284324300
C -0.6708048594 -1.0633647885 -0.4917073999
H -0.6708048594 -1.0633647885 -1.5827603999
H -1.7112621114 -1.0633645180 -0.1632992669
H -0.2227620889 -2.0024041473 -0.1632745516

8
1.40
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0910530000
H 1.0404571178 0.0000000000 -0.3284085581
H -0.4480430575 0.9390393681 -0.3284324300
C -0.6956494838 -1.1027486696 -0.5099187851
H -0.6956494838 -1.1027486696 -1.6009717851
H -1.7361067358 -1.1027483990 -0.1815106521
H -0.2476067134 -2.0417880283 -0.1814859368

8
1.45
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0910530000
H 1.0404571178 0.0000000000 -0.3284085581
H -0.4480430575 0.9390393681 -0.3284324300
C -0.7204941082 -1.1421325506 -0.5281301703
H -0.7204941082 -1.1421325506 -1.6191831703
H -1.7609513602 -1.1421322801 -0.1997220372
H -0.2724513378 -2.0811719094 -0.1996973220

8
1.50
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0910530000
H 1.0404571178 0.0000000000 -0.3284085581
H -0.4480430575 0.9390393681 -0.3284324300
C -0.7453387326 -1.1815164317 -0.5463415555
H -0.7453387326 -1.1815164317 -1.6373945555
H -1.7857959847 -1.1815161611 -0.2179334224
H -0.2972959622 -2.1205557904 -0.2179087071

8
1.55
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0910530000
H 1.0404571178 0.0000000000 -0.3284085581
H -0.4480430575 0.9390393681 -0.3284324300
C -0.7701833571 -1.2209003127 -0.5645529407
H -0.7701833571 -1.2209003127 -1.6556059407
H -1.8106406091 -1.2209000422 -0.2361448076
H -0.3221405866 -2.1599396715 -0.2361200923

8
1.60
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0910530000
H 1.0404571178 0.0000000000 -0.3284085581
H -0.4480430575 0.9390393681 -0.3284324300
C -0.7950279815 -1.2602841938 -0.5827643259
H -0.7950279815 -1.2602841938 -1.6738173259
```

```
H -1.8354852335 -1.2602839233 -0.2543561928
H -0.3469852111 -2.1993235525 -0.2543314775

8
1.65
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0910530000
H 1.0404571178 0.0000000000 -0.3284085581
H -0.4480430575 0.9390393681 -0.3284324300
C -0.8198726059 -1.2996680749 -0.6009757110
H -0.8198726059 -1.2996680749 -1.6920287110
H -1.8603298579 -1.2996678043 -0.2725675780
H -0.3718298355 -2.2387074336 -0.2725428627

8
1.70
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0910530000
H 1.0404571178 0.0000000000 -0.3284085581
H -0.4480430575 0.9390393681 -0.3284324300
C -0.8447172303 -1.3390519559 -0.6191870962
H -0.8447172303 -1.3390519559 -1.7102400962
H -1.8851744823 -1.3390516854 -0.2907789632
H -0.3966744599 -2.2780913146 -0.2907542479

8
1.75
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0910530000
H 1.0404571178 0.0000000000 -0.3284085581
H -0.4480430575 0.9390393681 -0.3284324300
C -0.8695618547 -1.3784358370 -0.6373984814
H -0.8695618547 -1.3784358370 -1.7284514814
H -1.9100191068 -1.3784355664 -0.3089903483
H -0.4215190843 -2.3174751957 -0.3089656331

8
1.80
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0910530000
H 1.0404571178 0.0000000000 -0.3284085581
H -0.4480430575 0.9390393681 -0.3284324300
C -0.8944064792 -1.4178197180 -0.6556098666
H -0.8944064792 -1.4178197180 -1.7466628666
H -1.9348637312 -1.4178194475 -0.3272017335
H -0.4463637087 -2.3568590768 -0.3271770182

8
1.85
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0910530000
H 1.0404571178 0.0000000000 -0.3284085581
H -0.4480430575 0.9390393681 -0.3284324300
C -0.9192511036 -1.4572035991 -0.6738212518
H -0.9192511036 -1.4572035991 -1.7648742518
H -1.9597083556 -1.4572033285 -0.3454131187
H -0.4712083332 -2.3962429578 -0.3453884034
```

```
8
1.90
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0910530000
H 1.0404571178 0.0000000000 -0.3284085581
H -0.4480430575 0.9390393681 -0.3284324300
C -0.9440957280 -1.4965874801 -0.6920326370
H -0.9440957280 -1.4965874801 -1.7830856370
H -1.9845529800 -1.4965872096 -0.3636245039
H -0.4960529576 -2.4356268389 -0.3635997886

8
1.95
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0910530000
H 1.0404571178 0.0000000000 -0.3284085581
H -0.4480430575 0.9390393681 -0.3284324300
C -0.9689403524 -1.5359713612 -0.7102440221
H -0.9689403524 -1.5359713612 -1.8012970221
H -2.0093976044 -1.5359710907 -0.3818358891
H -0.5208975820 -2.4750107199 -0.3818111738

8
2.00
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0910530000
H 1.0404571178 0.0000000000 -0.3284085581
H -0.4480430575 0.9390393681 -0.3284324300
C -0.9937849769 -1.5753552423 -0.7284554073
H -0.9937849769 -1.5753552423 -1.8195084073
H -2.0342422289 -1.5753549717 -0.4000472743
H -0.5457422064 -2.5143946010 -0.4000225590

8
2.10
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0910530000
H 1.0404571178 0.0000000000 -0.3284085581
H -0.4480430575 0.9390393681 -0.3284324300
C -1.0434742257 -1.6541230044 -0.7648781777
H -1.0434742257 -1.6541230044 -1.8559311777
H -2.0839314777 -1.6541227338 -0.4364700446
H -0.5954314553 -2.5931623631 -0.4364453293

8
2.20
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0910530000
H 1.0404571178 0.0000000000 -0.3284085581
H -0.4480430575 0.9390393681 -0.3284324300
C -1.0931634745 -1.7328907665 -0.8013009481
H -1.0931634745 -1.7328907665 -1.8923539481
H -2.1336207266 -1.7328904959 -0.4728928150
H -0.6451207041 -2.6719301252 -0.4728680997

8
2.30
C 0.0000000000 0.0000000000 0.0000000000
```

```
H 0.0000000000 0.0000000000 1.0910530000
H 1.0404571178 0.0000000000 -0.3284085581
H -0.4480430575 0.9390393681 -0.3284324300
C -1.1428527234 -1.8116585286 -0.8377237184
H -1.1428527234 -1.8116585286 -1.9287767184
H -2.1833099754 -1.8116582580 -0.5093155854
H -0.6948099530 -2.7506978873 -0.5092908701

8
2.40
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0910530000
H 1.0404571178 0.0000000000 -0.3284085581
H -0.4480430575 0.9390393681 -0.3284324300
C -1.1925419722 -1.8904262907 -0.8741464888
H -1.1925419722 -1.8904262907 -1.9651994888
H -2.2329992242 -1.8904260202 -0.5457383557
H -0.7444992018 -2.8294656494 -0.5457136404

8
2.50
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0910530000
H 1.0404571178 0.0000000000 -0.3284085581
H -0.4480430575 0.9390393681 -0.3284324300
C -1.2422312211 -1.9691940528 -0.9105692592
H -1.2422312211 -1.9691940528 -2.0016222592
H -2.2826884731 -1.9691937823 -0.5821611261
H -0.7941884506 -2.9082334115 -0.5821364108

8
2.60
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0910530000
H 1.0404571178 0.0000000000 -0.3284085581
H -0.4480430575 0.9390393681 -0.3284324300
C -1.2919204699 -2.0479618149 -0.9469920295
H -1.2919204699 -2.0479618149 -2.0380450295
H -2.3323777219 -2.0479615444 -0.6185838965
H -0.8438776995 -2.9870011737 -0.6185591812

8
2.70
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0910530000
H 1.0404571178 0.0000000000 -0.3284085581
H -0.4480430575 0.9390393681 -0.3284324300
C -1.3416097188 -2.1267295770 -0.9834147999
H -1.3416097188 -2.1267295770 -2.0744677999
H -2.3820669708 -2.1267293065 -0.6550066668
H -0.8935669483 -3.0657689358 -0.6549819515

8
2.80
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0910530000
H 1.0404571178 0.0000000000 -0.3284085581
H -0.4480430575 0.9390393681 -0.3284324300
```

```
C -1.3912989676 -2.2054973392 -1.0198375703
H -1.3912989676 -2.2054973392 -2.1108905703
H -2.4317562196 -2.2054970686 -0.6914294372
H -0.9432561972 -3.1445366979 -0.6914047219

8
2.90
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0910530000
H 1.0404571178 0.0000000000 -0.3284085581
H -0.4480430575 0.9390393681 -0.3284324300
C -1.4409882164 -2.2842651013 -1.0562603406
H -1.4409882164 -2.2842651013 -2.1473133406
H -2.4814454685 -2.2842648307 -0.7278522076
H -0.9929454460 -3.2233044600 -0.7278274923

8
3.10
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0910530000
H 1.0404571178 0.0000000000 -0.3284085581
H -0.4480430575 0.9390393681 -0.3284324300
C -1.5403667141 -2.4418006255 -1.1291058814
H -1.5403667141 -2.4418006255 -2.2201588814
H -2.5808239661 -2.4418003549 -0.8006977483
H -1.0923239437 -3.3808399842 -0.8006730330

8
3.30
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0910530000
H 1.0404571178 0.0000000000 -0.3284085581
H -0.4480430575 0.9390393681 -0.3284324300
C -1.6397452118 -2.5993361497 -1.2019514221
H -1.6397452118 -2.5993361497 -2.2930044221
H -2.6802024638 -2.5993358792 -0.8735432890
H -1.1917024414 -3.5383755085 -0.8735185737

8
3.50
C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0910530000
H 1.0404571178 0.0000000000 -0.3284085581
H -0.4480430575 0.9390393681 -0.3284324300
C -1.7391237095 -2.7568716740 -1.2747969628
H -1.7391237095 -2.7568716740 -2.3658499628
H -2.7795809615 -2.7568714034 -0.9463888298
H -1.2910809391 -3.6959110327 -0.9463641145
```

- CH_4 (equilibrium):

```
5

C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0883100000
H 1.0260649157 0.0000000000 -0.3627801605
H -0.5130521462 -0.8885870764 -0.3627797665
H -0.5130261191 0.8886085072 -0.3627670806
```

- C_2H_6 (equilibrium):

```
8

C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0910530000
H 1.0404571178 0.0000000000 -0.3284085581
H -0.4480430575 0.9390393681 -0.3284324300
C -0.7588263823 -1.2028971530 -0.5562281523
H -0.7588263823 -1.2028971530 -1.6472811523
H -1.7992836344 -1.2028968825 -0.2278200192
H -0.3107836119 -2.1419365118 -0.2277953039
```

- C_2H_4 (equilibrium):

```
6

C 0.0000000000 0.0000000000 0.0000000000
H 0.0000000000 0.0000000000 1.0825780000
H 0.9686785376 0.0000000000 -0.4833623713
C -1.1260810579 -0.0000000000 -0.6965844737
H -1.1260810579 -0.0000000000 -1.7791624737
H -2.0947595955 -0.0000000000 -0.2132221024
```

- C_2H_2 (equilibrium):

```
4

C -0.5980109316 0.0000000000 0.0000000000
H -1.6595966855 0.0000000000 0.0000000000
C 0.5980109403 0.0000000000 0.0000000000
H 1.6595966768 0.0000000000 0.0000000000
```

2 Table of energies reported in this work

- H_{10} ring model:

```
#bL E_rhf E_2to1 E_3to1 E_4to1 E_fci
0.50 -2.80415 -2.90726 -2.89268 -2.87803 -2.87495
0.55 -3.59215 -3.70280 -3.68709 -3.67199 -3.66882
0.60 -4.14669 -4.26475 -4.24828 -4.23276 -4.22949
0.65 -4.53771 -4.66298 -4.64621 -4.63031 -4.62688
0.70 -4.81141 -4.94369 -4.92708 -4.91084 -4.90719
0.75 -4.99926 -5.13841 -5.12240 -5.10586 -5.10194
0.80 -5.12332 -5.26933 -5.25433 -5.23752 -5.23328
0.85 -5.19943 -5.35249 -5.33886 -5.32179 -5.31719
0.90 -5.23915 -5.39963 -5.38770 -5.37041 -5.36539
0.95 -5.25101 -5.41951 -5.40962 -5.39211 -5.38662
1.00 -5.24139 -5.41872 -5.41121 -5.39349 -5.38746
1.05 -5.21511 -5.40229 -5.39753 -5.37960 -5.37294
1.10 -5.17587 -5.37414 -5.37254 -5.35439 -5.34702
1.15 -5.12656 -5.33738 -5.33941 -5.32102 -5.31282
1.20 -5.06951 -5.29455 -5.30073 -5.28206 -5.27290
1.25 -5.00659 -5.24775 -5.25865 -5.23963 -5.22937
1.30 -4.93935 -5.19874 -5.21498 -5.19548 -5.18397
1.35 -4.86907 -5.14900 -5.17123 -5.15104 -5.13813
1.40 -4.79680 -5.09975 -5.12863 -5.10743 -5.09299
1.45 -4.72343 -5.05204 -5.08819 -5.06547 -5.04942
1.50 -4.64967 -5.00667 -5.05065 -5.02568 -5.00807
1.60 -4.50332 -4.92536 -4.98605 -4.95333 -4.93357
1.70 -4.36135 -4.85873 -4.93601 -4.88989 -4.87104
1.80 -4.22616 -4.80716 -4.89823 -4.83385 -4.82035
1.90 -4.09923 -4.76908 -4.86823 -4.78528 -4.78044
2.00 -3.98140 -4.74187 -4.84126 -4.74589 -4.74978
2.10 -3.87301 -4.72925 -4.78646 -4.72543 -4.72672
2.20 -3.77403 -4.71804 -4.74062 -4.71242 -4.70964
2.30 -3.68417 -4.70645 -4.71340 -4.70114 -4.69716
2.40 -3.60298 -4.69645 -4.69649 -4.69211 -4.68812
2.50 -3.52992 -4.68845 -4.68573 -4.68374 -4.68161
```

- CH_4 dissociation:

```
#bL E_rhf E_2to1 E_3to1 E_2to1(NSC) E_3to1(NSC) E_1site(NSC) E_dmrg
0.70 -39.4573 -39.5162 -39.5226 -39.5025 -39.5221 -39.5329 -39.5255
0.75 -39.5448 -39.6076 -39.6112 -39.5917 -39.6107 -39.6219 -39.6141
0.80 -39.6088 -39.6748 -39.6764 -39.6572 -39.6759 -39.6872 -39.6792
0.85 -39.6546 -39.7231 -39.7235 -39.7045 -39.7230 -39.7344 -39.7262
0.90 -39.6864 -39.7568 -39.7566 -39.7378 -39.7561 -39.7677 -39.7593
0.95 -39.7073 -39.7793 -39.7790 -39.7602 -39.7785 -39.7901 -39.7817
1.00 -39.7199 -39.7931 -39.7929 -39.7741 -39.7925 -39.8041 -39.7958
1.05 -39.7258 -39.8001 -39.8004 -39.7814 -39.8001 -39.8117 -39.8034
1.10 -39.7266 -39.8017 -39.8028 -39.7836 -39.8026 -39.8142 -39.8061
1.15 -39.7233 -39.7991 -39.8012 -39.7818 -39.8012 -39.8128 -39.8049
1.20 -39.7168 -39.7932 -39.7966 -39.7768 -39.7967 -39.8083 -39.8007
1.25 -39.7079 -39.7848 -39.7896 -39.7694 -39.7899 -39.8015 -39.7942
1.30 -39.6970 -39.7743 -39.7808 -39.7601 -39.7814 -39.7930 -39.7861
1.35 -39.6846 -39.7622 -39.7706 -39.7493 -39.7715 -39.7831 -39.7767
1.40 -39.6711 -39.7489 -39.7595 -39.7375 -39.7607 -39.7723 -39.7664
1.45 -39.6568 -39.7347 -39.7477 -39.7249 -39.7493 -39.7608 -39.7556
1.50 -39.6418 -39.7199 -39.7354 -39.7118 -39.7375 -39.7490 -39.7444
1.55 -39.6265 -39.7046 -39.7229 -39.6985 -39.7255 -39.7370 -39.7332
```

```
1.60 -39.6109 -39.6891 -39.7104 -39.6850 -39.7136 -39.7249 -39.7220
1.65 -39.5952 -39.6735 -39.6980 -39.6717 -39.7019 -39.7129 -39.7111
1.70 -39.5795 -39.6580 -39.6858 -39.6585 -39.6904 -39.7012 -39.7005
1.75 -39.5640 -39.6426 -39.6739 -39.6457 -39.6794 -39.6897 -39.6903
1.80 -39.5486 -39.6275 -39.6624 -39.6334 -39.6689 -39.6786 -39.6806
1.85 -39.5334 -39.6127 -39.6515 -39.6216 -39.6589 -39.6679 -39.6715
1.90 -39.5186 -39.5984 -39.6411 -39.6104 -39.6496 -39.6576 -39.6630
1.95 -39.5041 -39.5847 -39.6314 -39.6000 -39.6410 -39.6477 -39.6552
2.00 -39.4900 -39.5716 -39.6223 -39.5902 -39.6330 -39.6383 -39.6480
2.10 -39.4631 -39.5475 -39.6061 -39.5731 -39.6193 -39.6208 -39.6355
2.20 -39.4381 -39.5264 -39.5926 -39.5590 -39.6083 -39.6049 -39.6254
2.30 -39.4151 -39.5084 -39.5817 -39.5478 -39.5998 -39.5904 -39.6175
2.40 -39.3940 -39.4932 -39.5730 -39.5390 -39.5933 -39.5770 -39.6115
2.50 -39.3749 -39.4806 -39.5663 -39.5319 -39.5882 -39.5648 -39.6070
2.60 -39.3575 -39.4701 -39.5610 -39.5261 -39.5842 -39.5535 -39.6037
2.70 -39.3419 -39.4614 -39.5570 -39.5212 -39.5808 -39.5432 -39.6012
2.80 -39.3280 -39.4541 -39.5540 -39.5169 -39.5780 -39.5340 -39.5995
2.90 -39.3155 -39.4481 -39.5516 -39.5131 -39.5756 -39.5257 -39.5982
```

- C_2H_6 dissociation

```
#bL E_rhf E_2to1 E_3to1 E_2to1(NSC) E_3to1(NSC) E_1site(NSC) E_dmrg
1.00 -77.7677 -77.9058 -77.8904 -77.8609 -77.8944 -77.9091 -77.9088
1.05 -77.9073 -78.0517 -78.0326 -78.0032 -78.0355 -78.0499 -78.0480
1.10 -78.0159 -78.1645 -78.1435 -78.1145 -78.1456 -78.1596 -78.1563
1.15 -78.0996 -78.2508 -78.2295 -78.2011 -78.2310 -78.2446 -78.2400
1.20 -78.1636 -78.3158 -78.2955 -78.2680 -78.2968 -78.3097 -78.3042
1.25 -78.2117 -78.3639 -78.3456 -78.3191 -78.3470 -78.3590 -78.3526
1.30 -78.2471 -78.3984 -78.3830 -78.3577 -78.3847 -78.3956 -78.3886
1.35 -78.2724 -78.4221 -78.4103 -78.3861 -78.4124 -78.4221 -78.4146
1.40 -78.2894 -78.4372 -78.4296 -78.4065 -78.4321 -78.4403 -78.4327
1.45 -78.2999 -78.4456 -78.4424 -78.4202 -78.4455 -78.4519 -78.4443
1.50 -78.3050 -78.4486 -78.4501 -78.4287 -78.4537 -78.4582 -78.4508
1.55 -78.3058 -78.4473 -78.4537 -78.4329 -78.4579 -78.4601 -78.4532
1.60 -78.3030 -78.4428 -78.4541 -78.4336 -78.4588 -78.4584 -78.4523
1.65 -78.2974 -78.4357 -78.4519 -78.4315 -78.4571 -78.4539 -78.4487
1.70 -78.2895 -78.4266 -78.4476 -78.4270 -78.4533 -78.4471 -78.4431
1.75 -78.2797 -78.4159 -78.4418 -78.4206 -78.4479 -78.4383 -78.4358
1.80 -78.2684 -78.4041 -78.4348 -78.4128 -78.4412 -78.4281 -78.4273
1.85 -78.2558 -78.3915 -78.4268 -78.4037 -78.4335 -78.4166 -78.4178
1.90 -78.2424 -78.3782 -78.4182 -78.3936 -78.4252 -78.4041 -78.4077
1.95 -78.2282 -78.3645 -78.4092 -78.3829 -78.4164 -78.3909 -78.3971
2.00 -78.2136 -78.3506 -78.3999 -78.3716 -78.4072 -78.3772 -78.3864
2.10 -78.1835 -78.3227 -78.3811 -78.3481 -78.3888 -78.3490 -78.3649
2.20 -78.1532 -78.2955 -78.3630 -78.3243 -78.3710 -78.3205 -78.3445
2.30 -78.1236 -78.2695 -78.3459 -78.3009 -78.3543 -78.2926 -78.3260
2.40 -78.0952 -78.2451 -78.3302 -78.2784 -78.3390 -78.2658 -78.3099
2.50 -78.0684 -78.2225 -78.3158 -78.2573 -78.3254 -78.2405 -78.2963
2.60 -78.0434 -78.2018 -78.3029 -78.2377 -78.3133 -78.2169 -78.2852
2.70 -78.0203 -78.1830 -78.2912 -78.2196 -78.3028 -78.1951 -78.2764
2.80 -77.9991 -78.1659 -78.2808 -78.2031 -78.2935 -78.1751 -78.2696
2.90 -77.9798 -78.1506 -78.2715 -78.1883 -78.2856 -78.1569 -78.2645
3.10 -77.9467 -78.1250 -78.2563 -78.1632 -78.2730 -78.1259 -78.2579
3.30 -77.9206 -78.1056 -78.2453 -78.1437 -78.2641 -78.1014 -78.2546
3.50 -77.9004 -78.0914 -78.2379 -78.1292 -78.2583 -78.0826 -78.2531
```

3 A Newton-Raphson Algorithm for solving the constrained optimization problem in Sec. III E

Here, we present a Newton-Raphson algorithm for performing the constrained optimization discussed in Sec. III E. We intend to make this algorithm generic so that it can be applied to any type of constraints (i.e., not have to be on-site densities/pair-densities).

Let $\hat{H}$ denote the Hamiltonian we are interested in. Let p index the (orthonormal) one-electron basis (i.e., the site basis). Now the task is to diagonalize $\hat{H}$ under the constraints that

$$P_{pq} = P^0_{pq}, \qquad \Gamma_{rstu} = \Gamma^0_{rstu}, \tag{1}$$

for some indices $p, q, \cdots, u$, where $\{P_{pq}\}$ and $\{\Gamma_{rstu}\}$ are elements of 1PDM and 2PDM obtained from diagonalizing $\hat{H}$, and $\{P^0_{pq}\}$ and $\{\Gamma^0_{rstu}\}$ are some given and fixed values. This problem is described by the following Lagrangian,

$$\begin{aligned}\mathcal{L}[\Psi; \{\lambda_{pq}\}, \{\Lambda_{rstu}\}] = \langle\Psi|\hat{H}|\Psi\rangle + \sum_{pq} \lambda_{pq}(\langle\Psi|a^\dagger_p a_q|\Psi\rangle - P^0_{pq}) + \\ \sum_{rstu} \Lambda_{rstu}(\langle\Psi|a^\dagger_r a^\dagger_s a_u a_t|\Psi\rangle - \Gamma^0_{rstu}) - \mathcal{E}(\langle\Psi|\Psi\rangle - 1)\end{aligned} \tag{2}$$

Making $\mathcal{L}$ stationary gives rise to the following eigenvalue equation,

$$(\hat{H} + \hat{v}^{\mathrm{c}})|\Psi\rangle = \mathcal{E}|\Psi\rangle, \tag{3}$$

where

$$\hat{v}^{\mathrm{c}} = \sum_{pq} \lambda_{pq} a^\dagger_p a_q + \sum_{rstu} \Lambda_{rstu} a^\dagger_r a^\dagger_s a_u a_t. \tag{4}$$

The derivation above indicates that one only needs to find a set of parameters $\{\lambda_{pq}\}$ and $\{\Lambda_{rstu}\}$ that make up the constraint potential $\hat{v}_{\mathrm{c}}$, such that the ground state of the dressed Hamiltonian, $\hat{H} + \hat{v}^{\mathrm{c}}$, satisfies the required constraints in eqn (1). The algorithm shown below uses the Newton-Raphson method to determine this constraint potential.

1. Input: $\hat{H}$, $\{P^0_{pq}\}$, $\{\Gamma^0_{rstu}\}$ (suppose there are n 1PDM constraints and m 2PDM constraints, respectively).

2. Initialize the constraint potential vector,

$$\boldsymbol{u} = \begin{bmatrix} \lambda_{pq} \\ \Lambda_{rstu} \end{bmatrix} \tag{5}$$

   to some reasonable values (e.g., all zeros). Note that $\boldsymbol{u}$ is of length $n + m$.

3. Compute the loss vector,

$$\boldsymbol{y} = \begin{bmatrix} P_{pq} - P^0_{pq} \\ \Gamma_{rstu} - \Gamma^0_{rstu} \end{bmatrix}, \tag{6}$$

   which is also a vector of length $n + m$.

4. Compute the Jacobian,

$$\boldsymbol{J} = \begin{bmatrix} \frac{\partial P_{pq}}{\partial \lambda_{pq}} & \frac{\partial P_{pq}}{\partial \Lambda_{rstu}} \\ \frac{\partial \Gamma_{rstu}}{\partial \lambda_{pq}} & \frac{\partial \Gamma_{rstu}}{\partial \Lambda_{rstu}} \end{bmatrix} \tag{7}$$

   where $\frac{\partial P_{pq}}{\partial \lambda_{pq}}$, $\frac{\partial P_{pq}}{\partial \Lambda_{rstu}}$, $\frac{\partial \Gamma_{rstu}}{\partial \lambda_{pq}}$, and $\frac{\partial \Gamma_{rstu}}{\partial \Lambda_{rstu}}$ are n-by-n, n-by-m, m-by-n, and m-by-m matrices.

5. Update the constraint potential vector $\boldsymbol{u}$. First compute the update vector,

$$\delta\boldsymbol{u} = -\boldsymbol{J}^{-1}\boldsymbol{y}. \tag{8}$$

   Then,

$$\boldsymbol{u} \leftarrow \boldsymbol{u} + \gamma\delta\boldsymbol{u}, \tag{9}$$

   where $\gamma \in \mathbb{R}$ is a scaling factor determined from line search.

6. Recompute the loss vector, $\boldsymbol{y}$, using the new constraint potential. Check if the constraints are satisfied,

$$\|\boldsymbol{y}\|_2 < \tau, \tag{10}$$

where τ is some given threshold (e.g., 10^{-6}).

7. If not, go back to step 4 until convergence is reached.

4 Comparison of site densities and pair-densities

In Sec. 4.2 of the main text, we compare the PESs of STO-3G CH_4 obtained by self-consistent (SC) and non-self-consistent (NSC) Incremental Embedding. Here we compare the quality of site densities and pair-densities derived from both methods in terms of RMS errors. In SC Incremental Embedding, both site densities and pair-densities are self-consistently determined according to Algorithm M1, while in NSC Incremental Embedding site-densities are constrained to the RHF values and pair-densities are determined based on that. The results are shown in Figure S1, from which we have three observations:

1. RHF site densities are of better quality compared to SC Incremental Embedding up to $3 \to 1$ level.
2. NSC pair-densities are of better quality compared to the SC counterparts.
3. For both NSC and SC, $3 \to 1$ improves $2 \to 1$ largely on both site densities and pair-densities.

5 Total correlation energies of small molecules in different basis sets

In Sec. 4.3 of the main text, we compare the performance of Incremental Embedding and one-site DMET in basis sets of increasing size in terms of total energy errors. Here we re-plot those figures in Figure S2 but in terms of total correlation energies. As mentioned in the main text, the correlation energies recovered by both Incremental Embedding and one-site DMET stop to increase when the basis set size reaches some point, while the exact correlation energies keep going up. From Figure S2 it is easy to see that this happens for Incremental Embedding when switching from 3-21G to 6-311G while occurring much earlier for one-site DMET. The good performance of Incremental Embedding in 6-311G is also an error cancellation by this phenomenon and the over-correlation by going from STO-3G to 3-21G.

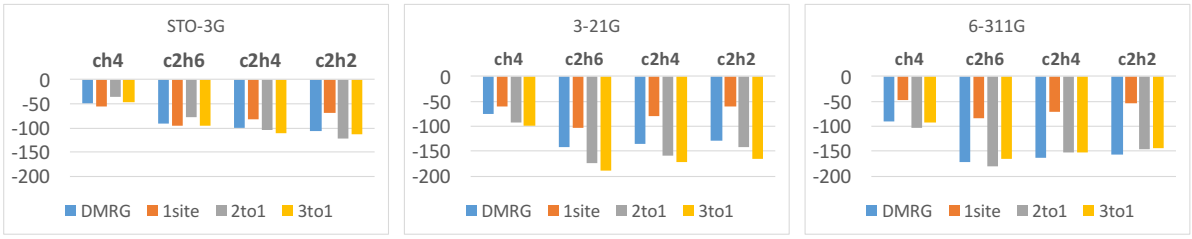

Figure S2: Re-plot of Figure M5 in terms of total correlation energies. Legend notation: 1site – 1-site DMET; 2to1 – $2 \to 1$ Incremental Embedding (NSC); 3to1 – $3 \to 1$ Incremental Embedding (NSC).

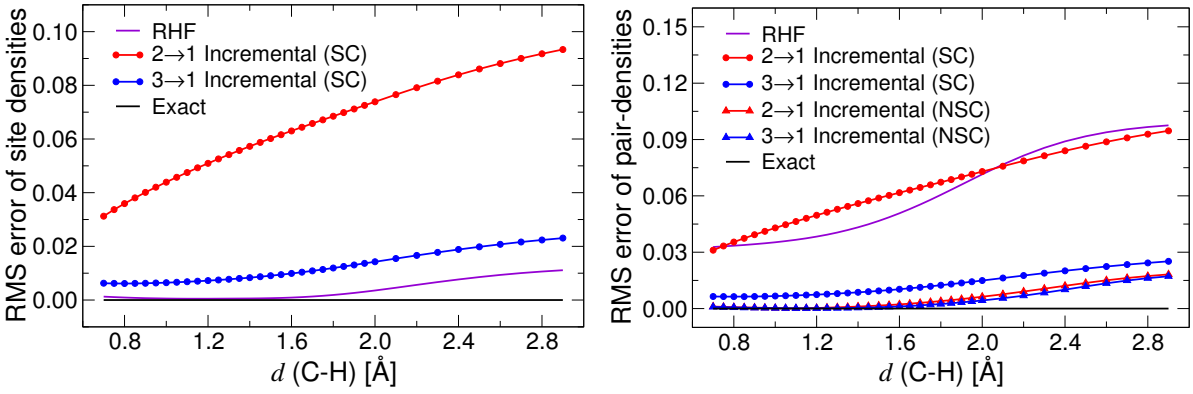

Figure S1: RMS error of site-densities (left) and pair-densities (right) of self-consistent (SC) and non-self-consistent (NSC) Incremental Embedding.