

Supplementary material: Energies from *ab initio* calculations (energy in Hartree, $T = 298.15$ K $p = 1$ atm).

H₂

E(ZPE)= 0.009725 E(Thermal)= 0.012086
E(SCF)= -1.131373 DE(MP2)= -0.027299
DE(CBS)= -0.006258 DE(MP34)= -0.00676
DE(Int)= 0.002474 DE(Empirical)= -0.012438
CBS-4 (0 K)= -1.171928 CBS-4 Energy= -1.16957
CBS-4 Enthalpy= -1.168624 CBS-4 Free Energy= -1.18340

C

E(ZPE)= 0 E(Thermal)= 0.001416
E(SCF)= -37.690198 DE(MP2)= -0.053996
DE(CBS)= -0.015706 DE(MP34)= -0.011266
DE(Int)= 0.004825 DE(Empirical)= -0.02191
CBS-4 (0 K)= -37.788251 CBS-4 Energy= -37.786835
CBS-4 Enthalpy= -37.785891 CBS-4 Free Energy= -37.802796

CH₃

E(ZPE)= 0.028441 E(Thermal)= 0.031608
E(SCF)= -39.573785 DE(MP2)= -0.13125
DE(CBS)= -0.035252 DE(MP34)= -0.016013
DE(Int)= 0.010357 DE(Empirical)= -0.042248 0.000709
CBS-4 (0 K)= -39.759749 CBS-4 Energy= -39.756582
CBS-4 Enthalpy= -39.755638 CBS-4 Free Energy= -39.779591

C₂H₅

E(ZPE)= 0.057942 E(Thermal)= 0.061973
E(SCF)= -78.621298 DE(MP2)= -0.275912
DE(CBS)= -0.073609 DE(MP34)= -0.027679
DE(Int)= 0.021227 DE(Empirical)= -0.079307 0.000388
CBS-4 (0 K)= -78.998637 CBS-4 Energy= -78.994606
CBS-4 Enthalpy= -78.993661 CBS-4 Free Energy= -79.022844

n-C₃H₇

E(ZPE)= 0.086447 E(Thermal)= 0.091444
E(SCF)= -117.66601 DE(MP2)= -0.422196
DE(CBS)= -0.110879 DE(MP34)= -0.038705
DE(Int)= 0.031972 DE(Empirical)= -0.116246
CBS-4 (0 K)= -118.235617 CBS-4 Energy= -118.23062
CBS-4 Enthalpy= -118.229676 CBS-4 Free Energy= -118.262402

i-C₃H₇

E(ZPE)= 0.086594 E(Thermal)= 0.091782
E(SCF)= -117.669944 DE(MP2)= -0.422239
DE(CBS)= -0.112029 DE(MP34)= -0.038983
DE(Int)= 0.032108 DE(Empirical)= -0.11633
CBS-4 (0 K)= -118.240823 CBS-4 Energy= -118.235635
CBS-4 Enthalpy= -118.234691 CBS-4 Free Energy= -118.267993

1-C₄H₉

E(ZPE)= 0.114511 E(Thermal)= 0.120794
E(SCF)= -156.710954 DE(MP2)= -0.568953
DE(CBS)= -0.148477 DE(MP34)= -0.049574
DE(Int)= 0.042682 DE(Empirical)= -0.153159
CBS-4 (0 K)= -157.473924 CBS-4 Energy= -157.467642
CBS-4 Enthalpy= -157.466698 CBS-4 Free Energy= -157.503174

2-C₄H₉

E(ZPE)= 0.11486 E(Thermal)= 0.121225
E(SCF)= -156.714704 DE(MP2)= -0.568701
DE(CBS)= -0.149402 DE(MP34)= -0.049552
DE(Int)= 0.04283 DE(Empirical)= -0.153256
CBS-4 (0 K)= -157.478326 CBS-4 Energy= -157.47196
CBS-4 Enthalpy= -157.471016 CBS-4 Free Energy= -157.508001

i-C₄H₉

E(ZPE)= 0.114413 E(Thermal)= 0.120538
E(SCF)= -156.710941 DE(MP2)= -0.570858
DE(CBS)= -0.148721 DE(MP34)= -0.049304
DE(Int)= 0.042783 DE(Empirical)= -0.153163
CBS-4 (0 K)= -157.475792 CBS-4 Energy= -157.469666
CBS-4 Enthalpy= -157.468722 CBS-4 Free Energy= -157.504467

t-C₄H₉

E(ZPE)= 0.114962 E(Thermal)= 0.121347
E(SCF)= -156.718933 DE(MP2)= -0.570515
DE(CBS)= -0.150033 DE(MP34)= -0.049739
DE(Int)= 0.042986 DE(Empirical)= -0.153253 -8.2E-05
CBS-4 (0 K)= -157.484525 CBS-4 Energy= -157.47814
CBS-4 Enthalpy= -157.477196 CBS-4 Free Energy= -157.513905

1-C₅H₁₁

E(ZPE)= 0.142565 E(Thermal)= 0.150164
E(SCF)= -195.755781 DE(MP2)= -0.715833
DE(CBS)= -0.185988 DE(MP34)= -0.060405
DE(Int)= 0.053418 DE(Empirical)= -0.190086
CBS-4 (0 K)= -196.712111 CBS-4 Energy= -196.704512
CBS-4 Enthalpy= -196.703568 CBS-4 Free Energy= -196.743697

2-C₅H₁₁

E(ZPE)= 0.142907 E(Thermal)= 0.150586
E(SCF)= -195.759608 DE(MP2)= -0.715518
DE(CBS)= -0.186967 DE(MP34)= -0.060803
DE(Int)= 0.053561 DE(Empirical)= -0.190186
CBS-4 (0 K)= -196.716613 CBS-4 Energy= -196.708935
CBS-4 Enthalpy= -196.70799 CBS-4 Free Energy= -196.748659

3-C₅H₁₁

E(ZPE)= 0.143106 E(Thermal)= 0.150685
E(SCF)= -195.759395 DE(MP2)= -0.715349
DE(CBS)= -0.186652 DE(MP34)= -0.060896
DE(Int)= 0.053541 DE(Empirical)= -0.190166
CBS-4 (0 K)= -196.715809 CBS-4 Energy= -196.70823
CBS-4 Enthalpy= -196.707286 CBS-4 Free Energy= -196.747969

2-methyl-but-1-yl (local minimum)

E(ZPE)= 0.142527 E(Thermal)= 0.149984
E(SCF)= -195.753992 DE(MP2)= -0.718742
DE(CBS)= -0.186626 DE(MP34)= -0.060108
DE(Int)= 0.053519 DE(Empirical)= -0.19005
CBS-4 (0 K)= -196.713472 CBS-4 Energy= -196.706015
CBS-4 Enthalpy= -196.705071 CBS-4 Free Energy= -196.744461

2-methyl-but-2-yl (rotated)

E(ZPE)= 0.143188 E(Thermal)= 0.150923
E(SCF)= -195.761274 DE(MP2)= -0.718018
DE(CBS)= -0.187903 DE(MP34)= -0.060681
DE(Int)= 0.053737 DE(Empirical)= -0.190194
CBS-4 (0 K)= -196.721144 CBS-4 Energy= -196.713409
CBS-4 Enthalpy= -196.712465 CBS-4 Free Energy= -196.753594

2-methyl-but-2-yl (local minimum)

E(ZPE)= 0.143377 E(Thermal)= 0.15098
E(SCF)= -195.762019 DE(MP2)= -0.718323
DE(CBS)= -0.187948 DE(MP34)= -0.060622
DE(Int)= 0.053741 DE(Empirical)= -0.190213
CBS-4 (0 K)= -196.722006 CBS-4 Energy= -196.714403
CBS-4 Enthalpy= -196.713459 CBS-4 Free Energy= -196.753662

2-methyl-but-2-yl (total minimum)

E(ZPE)= 0.143376 E(Thermal)= 0.150978
E(SCF)= -195.762019 DE(MP2)= -0.718326
DE(CBS)= -0.187949 DE(MP34)= -0.060622
DE(Int)= 0.053741 DE(Empirical)= -0.190213
CBS-4 (0 K)= -196.722012 CBS-4 Energy= -196.71441
CBS-4 Enthalpy= -196.713466 CBS-4 Free Energy= -196.753664

3-methyl-but-2-yl

E(ZPE)= 0.142871 E(Thermal)= 0.150388
E(SCF)= -195.759092 DE(MP2)= -0.718237
DE(CBS)= -0.187499 DE(MP34)= -0.060467
DE(Int)= 0.053667 DE(Empirical)= -0.190157
CBS-4 (0 K)= -196.718915 CBS-4 Energy= -196.711398
CBS-4 Enthalpy= -196.710454 CBS-4 Free Energy= -196.750353

3-methyl-but-1-yl

E(ZPE)= 0.142153 E(Thermal)= 0.149775
E(SCF)= -195.755204 DE(MP2)= -0.719008
DE(CBS)= -0.186681 DE(MP34)= -0.060003
DE(Int)= 0.053493 DE(Empirical)= -0.190058
CBS-4 (0 K)= -196.715309 CBS-4 Energy= -196.707687
CBS-4 Enthalpy= -196.706743 CBS-4 Free Energy= -196.746961

neopentyl

E(ZPE)= 0.141905 E(Thermal)= 0.149192
E(SCF)= -195.756148 DE(MP2)= -0.722158
DE(CBS)= -0.185761 DE(MP34)= -0.0595
DE(Int)= 0.053558 DE(Empirical)= -0.190016
CBS-4 -196.718119 CBS-4 Energy= -196.710833
CBS-4 Enthalpy= -196.709888 CBS-4 Free Energy= -196.748203

1-C₆H₁₁

E(ZPE)= 0.170581 E(Thermal)= 0.179535
E(SCF)= -234.80063 DE(MP2)= -0.862717
DE(CBS)= -0.223983 DE(MP34)= -0.071223
DE(Int)= 0.064179 DE(Empirical)= -0.227012
CBS-4 (0 K)= -235.950805 CBS-4 Energy= -235.94185
CBS-4 Enthalpy= -235.940906 CBS-4 Free Energy= -235.984708

2-C₆H₁₁

E(ZPE)= 0.170931 E(Thermal)= 0.179949
E(SCF)= -234.804439 DE(MP2)= -0.862385
DE(CBS)= -0.224847 DE(MP34)= -0.071632
DE(Int)= 0.064317 DE(Empirical)= -0.227115
CBS-4 (0 K)= -235.955169 CBS-4 Energy= -235.946152
CBS-4 Enthalpy= -235.945207 CBS-4 Free Energy= -235.989508

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3-C₆H₁₄

E(ZPE)= 0.171123 E(Thermal)= 0.180042
 E(SCF)= -234.804297 DE(MP2)= -0.862176
 DE(CBS)= -0.224828 DE(MP34)= -0.071741
 DE(Int)= 0.064294 DE(Empirical)= -0.227075
 CBS-4 (0 K)= -235.954702 CBS-4 Energy= -235.945782
 CBS-4 Enthalpy= -235.944838 CBS-4 Free Energy= -235.989208

2-methyl-1-pentyl

E(ZPE)= 0.17057 E(Thermal)= 0.179371
 E(SCF)= -234.798673 DE(MP2)= -0.865824
 DE(CBS)= -0.224766 DE(MP34)= -0.07091
 DE(Int)= 0.064311 DE(Empirical)= -0.226972
 CBS-4 (0 K)= -235.952264 CBS-4 Energy= -235.943464
 CBS-4 Enthalpy= -235.942519 CBS-4 Free Energy= -235.985552

2-methyl-2-pentyl

E(ZPE)= 0.171389 E(Thermal)= 0.180339
 E(SCF)= -234.807003 DE(MP2)= -0.86543
 DE(CBS)= -0.226221 DE(MP34)= -0.071423
 DE(Int)= 0.064555 DE(Empirical)= -0.227148
 CBS-4 (0 K)= -235.961281 CBS-4 Energy= -235.952332
 CBS-4 Enthalpy= -235.951388 CBS-4 Free Energy= -235.995238

2-methyl-3-pentyl

E(ZPE)= 0.171083 E(Thermal)= 0.179846
 E(SCF)= -234.803714 DE(MP2)= -0.865043
 DE(CBS)= -0.225294 DE(MP34)= -0.071387
 DE(Int)= 0.064431 DE(Empirical)= -0.227065
 CBS-4 (0 K)= -235.956999 CBS-4 Energy= -235.94823
 CBS-4 Enthalpy= -235.947282 CBS-4 Free Energy= -235.99089

4-methyl-2-pentyl

E(ZPE)= 0.170868 E(Thermal)= 0.179707
 E(SCF)= -234.803179 DE(MP2)= -0.866667
 DE(CBS)= -0.225847 DE(MP34)= -0.071153
 DE(Int)= 0.064481 DE(Empirical)= -0.227096
 CBS-4 (0 K)= -235.958593 CBS-4 Energy= -235.949755
 CBS-4 Enthalpy= -235.94881 CBS-4 Free Energy= -235.992284

4-methyl-1-pentyl

E(ZPE)= 0.170331 E(Thermal)= 0.179186
 E(SCF)= -234.799238 DE(MP2)= -0.866085
 DE(CBS)= -0.224615 DE(MP34)= -0.070809
 DE(Int)= 0.064324 DE(Empirical)= -0.22697
 CBS-4 (0 K)= -235.953062 CBS-4 Energy= -235.944207
 CBS-4 Enthalpy= -235.943263 CBS-4 Free Energy= -235.986516

3-methyl-1-pentyl

E(ZPE)= 0.170324 E(Thermal)= 0.179201
 E(SCF)= -234.798195 DE(MP2)= -0.866993
 DE(CBS)= -0.224581 DE(MP34)= -0.070768
 DE(Int)= 0.064301 DE(Empirical)= -0.226969
 CBS-4 (0 K)= -235.952881 CBS-4 Energy= -235.944004
 CBS-4 Enthalpy= -235.94306 CBS-4 Free Energy= -235.986256

3-methyl-2-pentyl

E(ZPE)= 0.170934 E(Thermal)= 0.179837
 E(SCF)= -234.801905 DE(MP2)= -0.866151
 DE(CBS)= -0.225665 DE(MP34)= -0.071262
 DE(Int)= 0.064467 DE(Empirical)= -0.227075
 CBS-4 (0 K)= -235.956658 CBS-4 Energy= -235.947754
 CBS-4 Enthalpy= -235.94681 CBS-4 Free Energy= -235.990443

3-methyl-3-pentyl

E(ZPE)= 0.171596 E(Thermal)= 0.180542
 E(SCF)= -234.804112 DE(MP2)= -0.866356
 DE(CBS)= -0.226083 DE(MP34)= -0.071593
 DE(Int)= 0.06451 DE(Empirical)= -0.2272
 CBS-4 (0 K)= -235.959239 CBS-4 Energy= -235.950293
 CBS-4 Enthalpy= -235.949349 CBS-4 Free Energy= -235.993913

2-ethyl-1-butyl

E(ZPE)= 0.170147 E(Thermal)= 0.179217
 E(SCF)= -234.798184 DE(MP2)= -0.866578
 DE(CBS)= -0.224298 DE(MP34)= -0.070876
 DE(Int)= 0.064277 DE(Empirical)= -0.227018
 CBS-4 (0 K)= -235.95253 CBS-4 Energy= -235.943459
 CBS-4 Enthalpy= -235.942515 CBS-4 Free Energy= -235.987061

2,3-dimethyl-1-butyl

E(ZPE)= 0.170086 E(Thermal)= 0.178931
 E(SCF)= -234.796767 DE(MP2)= -0.869509
 DE(CBS)= -0.224921 DE(MP34)= -0.070545
 DE(Int)= 0.064354 DE(Empirical)= -0.226957
 CBS-4 (0 K)= -235.954259 CBS-4 Energy= -235.945414
 CBS-4 Enthalpy= -235.94447 CBS-4 Free Energy= -235.987203

2,3-dimethyl-2-butyl

E(ZPE)= 0.171119 E(Thermal)= 0.180061
 E(SCF)= -234.805114 DE(MP2)= -0.868422
 DE(CBS)= -0.225997 DE(MP34)= -0.07108
 DE(Int)= 0.064542 DE(Empirical)= -0.227087
 CBS-4 (0 K)= -235.962039 CBS-4 Energy= -235.953098
 CBS-4 Enthalpy= -235.952153 CBS-4 Free Energy= -235.995729

3,3-dimethyl-1butyl

E(ZPE)= 0.16994 E(Thermal)= 0.178569
 E(SCF)= -234.799315 DE(MP2)= -0.871586
 DE(CBS)= -0.223762 DE(MP34)= -0.06997
 DE(Int)= 0.064231 DE(Empirical)= -0.226906 -0.000259
 CBS-4 -235.957367 CBS-4 Energy= -235.948739
 CBS-4 Enthalpy= -235.947795 CBS-4 Free Energy= -235.989482

C₂H₆

E(ZPE)= 0.073377 E(Thermal)= 0.076886
 E(SCF)= -79.251959 DE(MP2)= -0.310816
 DE(CBS)= -0.080654 DE(MP34)= -0.028722
 DE(Int)= 0.024081 DE(Empirical)= -0.086425
 CBS-4 (0 K)= -79.661117 CBS-4 Energy= -79.657608
 CBS-4 Enthalpy= -79.656664 CBS-4 Free Energy= -79.68426

propane

E(ZPE)= 0.101701 E(Thermal)= 0.10625
 E(SCF)= -118.296976 DE(MP2)= -0.457374
 DE(CBS)= -0.118041 DE(MP34)= -0.039594
 DE(Int)= 0.034828 DE(Empirical)= -0.12336 -0.000708
 CBS-4 (0 K)= -118.898816 CBS-4 Energy= -118.894267
 CBS-4 Enthalpy= -118.893323 CBS-4 Free Energy= -118.924501

i-bután

E(ZPE)= 0.12946 E(Thermal)= 0.135158
 E(SCF)= -157.342687 DE(MP2)= -0.606359
 DE(CBS)= -0.155926 DE(MP34)= -0.050078
 DE(Int)= 0.045657 DE(Empirical)= -0.160262 -0.000872
 CBS-4 (0 K)= -158.140196 CBS-4 Energy= -158.134498
 CBS-4 Enthalpy= -158.133554 CBS-4 Free Energy= -158.167797

neopentane

E(ZPE)= 0.156924 E(Thermal)= 0.163807
 E(SCF)= -196.388142 DE(MP2)= -0.757892
 DE(CBS)= -0.192937 DE(MP34)= -0.060108
 DE(Int)= 0.056421 DE(Empirical)= -0.197118 -0.00099
 CBS-4 -197.382853 CBS-4 Energy= -197.37597
 CBS-4 Enthalpy= -197.375026 CBS-4 Free Energy= -197.411894