Computationally efficient double hybrid density functional theory using dual basis methods

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Abstract

We examine the application of the recently developed dual basis methods of Head-Gordon and co-workers to double hybrid density functional computations. Using the B2-PLYP, B2GP-PLYP, DSD-BLYP and DSD-PBEP86 density functionals, we assess the performance of dual basis methods for the calculation of conformational energy changes in $\text{C}_4$-$\text{C}_7$ alkanes and for the S22 set of noncovalent interaction energies. The dual basis methods, combined with resolution-of-the-identity second-order Møller-Plesset theory, are shown to give results in excellent agreement with conventional methods at a much reduced computational cost.

Keywords: Double Hybrid Density Functional Theory, Dual Basis SCF, S22, ACONF, DFT benchmark

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The maximum deviation (MD) plotted against mean average deviation for our dual basis double hybrid DFT benchmark test set results.
INTRODUCTION

Improving Kohn-Sham density functional theory and many body perturbation theory by combining the two in some fashion is an attractive idea garnering much recent attention\textsuperscript{1,2}. Early difficulties in obtaining accurate results\textsuperscript{3} with Kohn-Sham (KS) orbitals and second Møller-Plesset (MP2) perturbation theory (many body perturbation theory with canonical self consistent field partitioning) were addressed with the development of so called double hybrid (DH) methods,\textsuperscript{4,6} where the idea is to use a mixture of Hartree-Fock (HF) and density functional theory (DFT) exchange with a portion of the correlation coming from DFT and the rest from an MP2 calculation using the resulting Kohn-Sham orbitals. This exchange-correlation partitioning is given by

\[ E_{XC} = (1 - c_x)E_{x}^{DFT} + c_x E_{x}^{HF} + c_c E_{c}^{DFT} + c_{os} E_{os}^{MP2} + c_{ss} E_{ss}^{MP2} + E_D \]  

where \( c_x \) is the amount of HF exchange, \( c_c \) is the amount of DFT correlation, \( c_{os} \) and \( c_{ss} \) are the mixing coefficients for the opposite (\( \alpha\beta \)) and same (\( \alpha\alpha \)) spin contributions to the MP2 correlation energy. The -D2 (2006) and -D3 (2010) Grimme dispersion correction\textsuperscript{7,8} is included within the \( E_D \) term as desired. For normal double hybrid methods such as B2-PLYP and B2GP-PLYP, the same spin and opposite spin coefficients are constrained to be equal. For DSD methods such as DSD-BLYP\textsuperscript{9} and DSD-PBEP86\textsuperscript{10} this constraint is lifted and the two components are optimized individually in the same manner as spin component scaled MP2 (SCS-MP2).\textsuperscript{6,11,12}

The improvement of DH methods over standard DFT functionals has been well documented\textsuperscript{13,14} for a wide variety of benchmark systems. This general applicability and accuracy is expected from the DH methods, with the added advantage of applicability to larger molecular systems where conventional wavefunction methods such as coupled cluster theory\textsuperscript{15} are impractical. Although second order Møller-Plesset perturbation theory is perhaps the simplest useful method for computing the post-SCF electron correlation energy, the formal \( O(n^5) \) computational scaling becomes a very significant bottleneck in large scale calculations. The application of DH methods to larger systems quickly reach this scaling bottleneck, resulting in the demand for an alternative. Similarly, the performance of the DFT portion of the calculation demands an improvement due to scaling with system size. The purpose of this
paper is to describe our proposed methodological changes to circumvent the scaling limitations in standard DH methods. Firstly, we address the computational cost of standard DFT calculations by performing a dual basis self consistent field (SCF) calculation. Following this the computational cost of the MP2 portion of the calculation is reduced by using the resolution-of-the-identity approximation.

The dual basis approach of Head-Gordon and co-workers is a method for reducing the computational cost of large basis SCF calculations. An SCF calculation in a small basis set is iterated to convergence, providing the small basis energy $E_S$ and molecular orbital (MO) coefficients $C_S$. Approximate large basis MO coefficients $C_L$ are obtained by projection of the small basis MO coefficients $C_S$ onto the large basis, found by solving the linear equations

$$S_L C_L = S_{LS} C_S$$

where $S_L$ is the large basis overlap matrix and $S_{LS}$ is the rectangular overlap matrix between the large and small basis. Using the projected orbitals, a new density matrix $P$ is formed, and a new Fock matrix, $F(P)$, is constructed and diagonalized, providing a new density $P'$. The density difference $\Delta P = P - P'$ is then used to compute a correction to the small basis SCF energy from

$$\Delta E_L = \text{Tr}[\Delta P F(P)],$$

and the dual basis SCF energy is obtained from

$$E_{DB} = E_S + \Delta E_L.$$

In this work we combine the dual basis SCF method with resolution-of-the-identity second-order Møller-Plesset theory. The conventional expression for the MP2 correlation energy is

$$E_{MP2} = - \sum_{ijab} (ia|jb)[2(ia|jb) - (ib|ja)]$$

where $\epsilon_q$ are the SCF orbital eigenvalues and the indices $i, j (a, b)$ range over occupied (virtual) molecular orbitals. The occupied-virtual MOs are obtained from a four index transformation of the AO basis electron repulsion integrals (ERIs)

$$(ia|jb) = \sum_{\sigma} C_{\sigma b} \sum_{\lambda} C_{\lambda j} \sum_{\nu} C_{\nu a} \sum_{\mu} C_{\mu i}(\mu \nu | \lambda \sigma)$$
where greek indices range over AOs and $C_{\nu i}$ are MO coefficients. Resolution-of-the-identity methods seek to replace the ERIs

$$(\mu\nu|\lambda\sigma) = \int dr_1 \int dr_2 \phi_\mu(r_1)\phi_\nu(r_1) \frac{1}{r_{12}} \phi_\lambda(r_2)\phi_\sigma(r_2)$$  \tag{7}

by a sum of two and three center integrals

$$(\mu\nu|\lambda\sigma) \approx \sum_{lm} (\mu\nu|l)(l|m)^{-1}(m|\lambda\sigma)$$  \tag{8}

where $l, m$ are the indices of auxiliary basis functions. In practice, the size of the auxiliary basis is typically 3-4 times larger than the primary basis, leading to large speedups in the ERI calculation and subsequent integral transformation.

We note that MP2 calculations using dual basis SCF orbitals formally have a singles contribution as the large basis density is not completely relaxed and Brillouin’s theorem therefore does not hold. However Steele et al.\cite{18} have shown that the contribution of the singles term is very small, therefore it is neglected in this work.

**METHODOLOGY**

The large basis set used for dual basis calculations in this work are the standard correlation consistent Dunning\cite{21-26} triple zeta basis sets with (aug-cc-pVTZ) and without (cc-pVTZ) diffuse functions. The corresponding small basis sets are pruned sets from these the larger (aug-) cc-pVTZ basis sets using the prescription given by Steele et al.\cite{18,20} which we denote r-cc-pVTZ and r-aug-cc-pVTZ in this paper. For r-cc-pVTZ only the $f$ functions are dropped, except in the case of hydrogen and helium where in addition to the $s$ functions the tightest $p$ function is kept. The pruning scheme is similar for the r-aug-cc-pVTZ set where in addition to the $f$ functions being dropped, the diffuse $d$ is also dropped. In the hydrogen and helium set all $s$ functions are kept as well as the two tightest $p$ functions, all others are dropped. In all RIMP2 calculations, we used the fitting basis sets from Weigend et al.\cite{27} For all DFT calculations in this work we make use of the so called JANS=2 grid in GAMESS, which is a 155 radial Euler-MacLaurin quadrature and pruned 974 point Lebedev grid. Tests with a larger grid did not lead to any appreciable differences in either conformer or dissociation energies.
To assess the usefulness of using dual basis SCF in a DH method, we make use of the S22 set of non-covalently bonded molecules and the ACONF set of alkane (C₄-C₆) conformers. Reference geometries and ab initio dissociation energies for the S22 are taken from Jurečka et al. and Takatani et al. respectively. For the ACONF set both reference geometries and ab initio conformer energies are taken from Gruzman et al. Dissociation and conformer energies were computed within the frozen core approximation (core-valence energy is implicit within the DFT framework, but is explicitly excluded from the MP2 correlation energy) as is usual for these sets. All electronic structure calculations in this work were done using a locally modified version of the GAMESS quantum chemistry program package in which we have implemented the dual basis SCF scheme outlined in the introduction. Throughout this paper we use RMS to mean “root mean square,” MAD to mean “mean average deviation,” and MD to mean “maximum deviation.”

RESULTS

ALKANE CONFORMER ORDER AND RELATIVE ENERGIES

The DB-RIDH results for the ACONF set of C₄-C₆ alkanes are presented in Tables 1 and 2 with and without the Grimme dispersion correction. Our reference ab initio data for the ACONF set comes from the W1h-val results of Gruzman et al. The W1h-val method incorporates SCF and CCSD(T) (coupled cluster with perturbative singles and doubles with perturbative triples) methods where the final SCF and CCSD energies are obtained using W2 extrapolation from the cc-pVT,QZ basis sets and the (T) contribution extrapolated from the cc-pVD,TZ basis set. In addition to the now standard ACONF set, we have also computed the conformer energies for n-heptane; the results can be found in Tables 3 and 4. The ab initio n-heptane results from Gruzman et al. are at the slightly lower MP2:CC level of theory (MP2/cc-pVQZ + [CCSD(T)/cc-pVDZ - MP2/cc-pVDZ] at a MP2/cc-pVDZ reference geometry). For n-butane through n-hexane (the ACONF set) the differences between W1h-val and MP2:CC are reported to be on the order of 0.01 kcal/mol, which is

Results for even longer alkane chains can be found in Byrd et al.
more than sufficiently accurate for our purposes. We find the RMS and MAD relative to the \textit{ab initio}\footnote{It should be noted that the energy difference between the \(G^+T^+G^-\) and GGG conformers is 0.05 kcal/mol, the smallest of the test set.} values to be around 0.5 kcal/mol for all functionals used, with almost a factor of two improvement for the DSD methods over the standard B2-PLYP. Incuding Grimme dispersion further improves the results to obtain nearly indistinguishable values compared to \textit{ab initio}. As expected for alkane conformers, the differences between the cc-pVTZ and the diffuse aug-cc-pVTZ basis sets are negligible.

The energetic ordering of each conformer is as important as the relative energies. For both basis sets the DH methods predict the same conformer ACONF ordering excluding the \(G^+T^+G^-\)GGG conformers\footnote{It should be noted that the energy difference between the \(G^+T^+G^-\) and GGG conformers is 0.05 kcal/mol, the smallest of the test set.}. Only the DSD methods including Grimme dispersion agree with the \textit{ab initio} ordering when using the cc-pVTZ basis set. Including diffuse functions with the aug-cc-pVTZ basis set brings every DH method into agreement with \textit{ab initio} so long as Grimme dispersion is included. This same conformer ordering error is seen in standard DH calculations\footnote{It should be noted that the energy difference between the \(G^+T^+G^-\) and GGG conformers is 0.05 kcal/mol, the smallest of the test set.} and so is not an indication of a problem with either using dual basis or RIMP2. For the case of n-heptane, the DB-RIDH calculations with and without Grimme dispersion have small number of non-systematic conformer ordering discrepancies. As the magnitude of the error in these discrepancies (errors near 0.01 kcal/mol) are the same size as the reported errors in MP2:CC we do not attach any particular significance to the differences in conformer ordering.

\textbf{S22 NON-COVALENT INTERACTION ENERGIES}

Tables 5 and 6 show the DB-RIHD results (with and without Grimme dispersion) for the S22 set of non-covalently bonded molecules. In the absence of a dispersion correction, the RMS and MAD values for both the cc-pVTZ and aug-cc-pVTZ basis sets relative to the benchmark CBS(\(\Delta\alpha(DT)Z\)) \textit{ab initio} results\footnote{It should be noted that the energy difference between the \(G^+T^+G^-\) and GGG conformers is 0.05 kcal/mol, the smallest of the test set.} range from 1 to 3 kcal/mol with the DSD methods performing the best overall. Inclusion of Grimme dispersion brings the agreement for all DH methods to better than half a kcal/mol for the cc-pVTZ basis set. As expected considering the number of polar molecules included within the S22 set, the inclusion of diffuse functions in the aug-cc-pVTZ basis reduces the RMS and MAD error even more.
All DH methods and further dispersion corrections are parameterized methods that are optimized using various test sets often employing QZ level basis sets or TZ level basis sets other than the Dunning type correlation sets (such as the PC-n and def2 basis sets). As such, care must be made when using basis sets other than the ones used for parametrization. The DH benchmark S22 calculations of Goerigk et al. give MAD and RMS values of 0.27 and 0.33 kcal/mol for B2-PLYP-D3/def2-QZVPP and 0.28 and 0.34 kcal/mol for DSD-BLYP-D3/def2-QZVPP. Our own MAD and RMS values of 0.36 and 0.48 kcal/mol for B2-PLYP-D3/c-pVTZ and 0.36 and 0.46 kcal/mol for DSD-BLYP-D3/cc-pVTZ are then entirely acceptable. It should be noted that our results of 0.16 and 0.21 kcal/mol for B2-PLYP-D3/aug-cc-pVTZ and 0.09 and 0.13 kcal/mol for DSD-BLYP-D3/aug-cc-pVTZ are a marked improvement over not only the cc-pVTZ results but also the benchmark def2-QZVPP Goerigk et al. values, illustrating the need for diffuse functions to accurately describe non-covalent bonds involving polar molecules.

CONCLUSIONS

We have shown that the use of dual basis and resolution-of-the-identity methods can speed up double hybrid DFT computations without significant loss in accuracy. Results are presented for alkane conformational energy differences and non-covalent interaction energies using the B2-PLYP, B2GP-PLYP, DSD-BLYP and DSD-PBEP86 double hybrid density functionals.

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References

1. A. Göring and M. Levy, Phys. Rev. B 47, 105 (1993).
2. A. Göring and M. Levy, Phys. Rev. A 50, 196 (1994).
3. R. J. Bartlett, V. F. Lotrich, and I. V. Schweigert, J. Chem. Phys. 123, 062205 (2005).
4. S. Grimme, J. Chem. Phys. 124, 034108 (2006).
5. P. Verma and R. J. Bartlett, J. Chem. Phys. 137, 134102 (2012).
6. T. Schwabe and S. Grimme, Acc. Chem. Res. 41, 569 (2008).
7. S. Grimme, J. Comput. Chem. 27, 1787 (2006).
8. S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, J. Chem. Phys. 132, 154104 (2010).
9. S. Kozuch, D. Gruzman, and J. M. L. Martin, J. Phys. Chem. C 114, 20801 (2010).
10. S. Kozuch and J. M. L. Martin, Phys. Chem. Chem. Phys. 13, 20104 (2011).
11. S. Grimme, J. Chem. Phys. 118, 9095 (2003).
12. Á. Szabados, J. Chem. Phys. 125, 214105 (2006).
13. L. Goerigk and S. Grimme, J. Chem. Theory Comput. 6, 107 (2010).
14. L. Goerigk and S. J. Grimme, J. Chem. Theory Comput. 7, 291 (2011).
15. R. J. Bartlett and M. Musial, Rev. Mod. Phys. 79, 291 (2007).
16. W. Liang and M. Head-Gordon, J. Phys. Chem. A 108, 3206 (2004).
17. M. Feyereisen, G. Fitzgerald, and A. Komornicki, Chem. Phys. Lett. 208, 359 (1993).
18. R. P. Steele, R. A. DiStasio, Y. Shao, J. Kong, and M. Head-Gordon, J. Chem. Phys. 125, 074108 (2006).
19. R. P. Steele and M. Head-Gordon, Mol. Phys. 105, 2455 (2007).
20. R. P. Steele, R. A. DiStasio, and M. Head-Gordon, J. Chem. Theory Comput. 5, 1560 (2009).

21. T. H. Dunning Jr., J. Chem. Phys. 90, 1007 (1989).

22. R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, J. Chem. Phys. 96, 6796 (1992).

23. D. E. Woon and T. H. Dunning Jr., J. Chem. Phys. 98, 1358 (1993).

24. D. E. Woon and T. H. Dunning Jr., J. Chem. Phys. 100, 2975 (1994).

25. D. E. Woon and T. H. Dunning, Jr., J. Chem. Phys. 103, 4572 (1995).

26. A. Wilson, T. van Mourik, and T. H. Dunning, Jr., J. Mol. Struct.: THEOCHEM 339, 338 (1996).

27. F. Weigend, A. Köhn, and C. Hättig, J. Chem. Phys. 116, 175 (2002).

28. P. Jurečka, J. Šponer, J. Černý, and P. Hobza, Phys. Chem. Chem. Phys. 8, 1985 (2006).

29. D. Gruzman, A. Karton, and J. M. L. Martin, J. Phys. Chem. A 113, 11974 (2009).

30. T. Takatani, E. G. Hohenstein, M. Malagoli, M. S. Marshall, and C. D. Sherrill, J. Chem. Phys. 132, 144104 (2010).

31. M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. J. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, J. A. Montgomery, Jr., J. Comput. Chem. 14, 1347 (1993).

32. M. S. Gordon and M. W. Schmidt, in Theory and Applications of Computational Chemistry, the first forty years, edited by C. E. Dykstra, G. Frenking, K. S. Kim, and G. E. Scuseria (Elsevier, Amsterdam, 2005), p. 1167.

33. J. A. Pople, M. Head-Gordon, and K. Raghavachari, J. Chem. Phys. 87, 5968 (1987).

34. J. N. Byrd, R. J. Bartlett, and J. A. Montgomery Jr., J. Phys. Chem. A 118, 1706 (2014).
35. A. Karton, A. Tarnopolsky, J.-F. Lameére, G. C. Schatz, and J. M. L. Martin, J. Phys. Chem. A 112, 12868 (2008).

36. F. Jensen, J. Chem. Phys. 115, 9113 (2001).

37. F. Jensen, J. Chem. Phys. 116, 7372 (2002).

38. F. Weigend, F. Furche, and R. Ahlrichs, J. Chem. Phys. 119, 12753 (2003).

39. F. Weigend and R. Ahlrichs, Phys. Chem. Chem. Phys. 7, 3297 (2005).
Table 1: Dual basis resolution-of-the-identity double hybrid cc-pVTZ conformer energies for the ACONF C₄-C₆ test set in kcal/mol. \textit{Ab initio} reference energies are the W1h-val values from Gruzman \textit{et al.} ²⁹

| cc-pVTZ    | B2-PLYP | B2GP-PLYP | DSD-BLYP | DSD-PBE\textit{P}86 | \textit{ab initio} |
|------------|---------|-----------|----------|---------------------|-------------------|
|            | −D3     | −D3       | −D3      | −D3                 | ab initio         |
| n-butane   |         |           |          |                     |                   |
| T          | 0.00    | 0.00      | 0.00     | 0.00                | 0.00              |
| G          | 0.79    | 0.66      | 0.74     | 0.66                | 0.68              |
|            | 0.64    | 0.68      | 0.54     | 0.60                |                   |
| n-pentane  |         |           |          |                     |                   |
| TT         | 0.00    | 0.00      | 0.00     | 0.00                | 0.00              |
| TG         | 0.81    | 0.66      | 0.76     | 0.66                | 0.69              |
| GG         | 1.51    | 1.08      | 1.37     | 1.07                | 1.19              |
| GX⁻        | 3.30    | 2.91      | 3.22     | 2.96                | 3.15              |
|            | 2.91    | 3.05      | 2.68     | 2.81                |                   |
| n-hexane   |         |           |          |                     |                   |
| TTT        | 0.00    | 0.00      | 0.00     | 0.00                | 0.00              |
| GTT        | 0.80    | 0.64      | 0.75     | 0.64                | 0.68              |
| TGT        | 0.81    | 0.65      | 0.76     | 0.65                | 0.69              |
| TGG        | 1.54    | 1.04      | 1.38     | 1.04                | 1.18              |
| GTG        | 1.61    | 1.27      | 1.50     | 1.27                | 1.35              |
| G⁺T⁺G⁻⁻    | 1.67    | 1.39      | 1.58     | 1.40                | 1.35              |
|            | 1.46    | 1.13      | 1.30     |                     |                   |
| GGG        | 2.23    | 1.43      | 1.96     | 1.42                | 1.66              |
| G⁺X⁻⁻T⁺⁺   | 3.19    | 2.74      | 3.09     | 2.78                | 2.90              |
| T⁺⁺G⁺X⁻⁻   | 3.26    | 2.83      | 3.16     | 2.87                | 2.98              |
| G⁺X⁻⁻G⁻⁻   | 4.01    | 3.45      | 3.87     | 3.50                | 3.63              |
| X⁺⁻G⁻⁻X⁺⁻  | 3.99    | 3.19      | 3.80     | 3.26                | 3.51              |
|            | 2.80    | 3.08      |          |                     |                   |
| X⁺⁺G⁻⁻X⁺⁺  | 5.85    | 5.06      | 5.69     | 5.16                | 5.39              |
|            | 4.64    | 4.93      |          |                     |                   |
| RMS        | 0.59    | 0.11      | 0.46     | 0.14                | 0.37              |
|            | 0.07    | 0.27      | 0.19     |                     |                   |
| MAD        | 0.52    | 0.10      | 0.41     | 0.12                | 0.33              |
|            | 0.06    | 0.24      | 0.17     |                     |                   |
| MD         | 0.98    | 0.18      | 0.77     | 0.24                | 0.64              |
|            | 0.15    | 0.47      | 0.29     |                     |                   |
Table 2: Dual basis resolution-of-the-identity double hybrid aug-cc-pVTZ conformer energies for the ACONF $C_4$-$C_6$ test set in kcal/mol. *Ab initio* reference energies are the W1h-val values from Gruzman *et al.*

|       | aug-cc-pVTZ | B2-PLYP $-D_3$ | B2GP-PLYP $-D_3$ | DSD-BLYP $-D_3$ | DSD-PBEP86 $-D_3$ | ab initio | n-butane |
|-------|-------------|----------------|------------------|-----------------|------------------|-----------|----------|
|       |             |                 |                  |                 |                  |           |          |
| T     | 0.00        | 0.00            | 0.00             | 0.00            | 0.00             | 0.00      | 0.00     |
| G     | 0.79        | 0.66            | 0.74             | 0.65            | 0.71             | 0.63      | 0.68     | 0.53 | 0.60 |
|       |             |                 |                  |                 |                  |           |          |
|       |             |                 |                  |                 |                  |           |          |
| TT    | 0.00        | 0.00            | 0.00             | 0.00            | 0.00             | 0.00      | 0.00     |
| TG    | 0.80        | 0.66            | 0.75             | 0.65            | 0.72             | 0.63      | 0.68     | 0.52 | 0.61 |
| GG    | 1.49        | 1.05            | 1.34             | 1.04            | 1.25             | 0.97      | 1.15     | 0.75 | 0.96 |
| GX$^-$| 3.27        | 2.88            | 3.18             | 2.92            | 3.11             | 2.86      | 3.00     | 2.63 | 2.81 |
|       |             |                 |                  |                 |                  |           |          |
| TTT   | 0.00        | 0.00            | 0.00             | 0.00            | 0.00             | 0.00      | 0.00     |
| GTT   | 0.79        | 0.63            | 0.74             | 0.63            | 0.70             | 0.66      | 0.66     | 0.49 | 0.60 |
| TGT   | 0.81        | 0.65            | 0.75             | 0.64            | 0.72             | 0.61      | 0.68     | 0.50 | 0.60 |
| TGG   | 1.51        | 1.01            | 1.34             | 1.00            | 1.24             | 0.93      | 1.13     | 0.69 | 0.93 |
| GTG   | 1.59        | 1.25            | 1.48             | 1.25            | 1.40             | 1.18      | 1.32     | 0.97 | 1.18 |
| G$^+$T$^+$G$^-$ | 1.66      | 1.38            | 1.56             | 1.38            | 1.50             | 1.33      | 1.43     | 1.10 | 1.30 |
| GGG   | 2.17        | 1.37            | 1.90             | 1.36            | 1.74             | 1.23      | 1.58     | 0.88 | 1.25 |
| G$^+$X$^-$T$^+$ | 3.15      | 2.69            | 3.04             | 2.73            | 2.95             | 2.67      | 2.84     | 2.42 | 2.63 |
| T$^+$G$^+$X$^-$ | 3.23      | 2.79            | 3.12             | 2.83            | 3.04             | 2.77      | 2.93     | 2.52 | 2.74 |
| G$^+$X$^-$G$^-$ | 3.97      | 3.40            | 3.82             | 3.44            | 3.70             | 3.35      | 3.55     | 2.99 | 3.28 |
| X$^+$G$^-$G$^-$ | 3.94      | 3.13            | 3.73             | 3.19            | 3.59             | 3.08      | 3.42     | 2.71 | 3.08 |
| X$^+$G$^-$X$^+$ | 5.78      | 4.99            | 5.61             | 5.08            | 5.47             | 4.98      | 5.29     | 4.53 | 4.93 |
|       | RMS         | 0.55            | 0.07             | 0.42             | 0.09             | 0.32      | 0.03     | 0.21 | 0.24 |
|       | MAD         | 0.50            | 0.07             | 0.37             | 0.09             | 0.29      | 0.02     | 0.19 | 0.22 |
|       | MD          | 0.92            | 0.12             | 0.68             | 0.16             | 0.54      | 0.07     | 0.36 | 0.39 |
Table 3: Dual basis resolution-of-the-identity double hybrid cc-pVTZ conformer energies for the n-heptane conformers in kcal/mol. *Ab initio* reference energies are the MP2:CC values from Gruzman *et al*. 29

| n-heptane | cc-pVTZ | B2-PLYP | B2GP-PLYP | DSD-BLYP | DSD-PBEP86 | *ab initio* |
|-----------|---------|---------|-----------|-----------|-------------|-------------|
| TTTT      | -D3     | -D3     | -D3       | -D2       |              |             |
| TTTG⁻     | 0.00    | 0.00    | 0.00      | 0.00      | 0.00         | 0.00         |
| TTG⁻T     | 0.78    | 0.62    | 0.73      | 0.70      | 0.60         | 0.67         | 0.51     | 0.59         |
| TTG⁻G⁻    | 0.79    | 0.61    | 0.73      | 0.70      | 0.59         | 0.66         | 0.49     | 0.57         |
| TG⁺G⁺T     | 1.47    | 0.96    | 1.31      | 0.97      | 1.22         | 0.90         | 1.13     | 0.70         | 0.90         |
| TG⁺TG⁺     | 1.58    | 1.23    | 1.47      | 1.23      | 1.40         | 1.18         | 1.33     | 0.99         | 1.14         |
| G⁺TTG⁺     | 1.55    | 1.23    | 1.45      | 1.23      | 1.39         | 1.19         | 1.32     | 1.01         | 1.16         |
| G⁺TTG⁻     | 1.56    | 1.24    | 1.47      | 1.25      | 1.40         | 1.20         | 1.34     | 1.02         | 1.17         |
| TG⁺TG⁻     | 1.65    | 1.36    | 1.57      | 1.38      | 1.51         | 1.33         | 1.45     | 1.13         | 1.29         |
| TG⁺G⁺G⁺    | 2.11    | 1.31    | 1.86      | 1.32      | 1.72         | 1.22         | 1.58     | 0.92         | 1.22         |
| G⁺TG⁺G⁺    | 2.22    | 1.53    | 2.01      | 1.54      | 1.88         | 1.45         | 1.75     | 1.16         | 1.44         |
| G⁺TG⁺G⁻    | 2.30    | 1.71    | 2.12      | 1.73      | 2.02         | 1.64         | 1.90     | 1.35         | 1.64         |
| G⁺G⁺G⁺G⁺   | 2.76    | 1.70    | 2.43      | 1.70      | 2.25         | 1.57         | 2.05     | 1.17         | 1.55         |
| TTX⁻G⁺     | 3.15    | 2.69    | 3.05      | 2.75      | 2.98         | 2.69         | 2.87     | 2.48         | 2.63         |
| TTX⁻X⁺     | 3.20    | 2.75    | 3.10      | 2.81      | 3.03         | 2.75         | 2.93     | 2.54         | 2.71         |
| TG⁺X⁻T     | 3.10    | 2.62    | 2.99      | 2.67      | 2.91         | 2.61         | 2.80     | 2.39         | 2.56         |
| TG⁺G⁺X⁻    | 3.88    | 3.02    | 3.68      | 3.10      | 3.55         | 3.00         | 3.38     | 2.67         | 2.96         |
| TX⁺G⁺G⁻    | 3.78    | 2.97    | 3.59      | 3.05      | 3.46         | 2.96         | 3.31     | 2.63         | 2.92         |
| G⁺TX⁺G⁻    | 3.97    | 3.32    | 3.82      | 3.39      | 3.71         | 3.31         | 3.56     | 2.99         | 3.21         |
| G⁺TG⁺X⁻    | 4.00    | 3.40    | 3.86      | 3.46      | 3.75         | 3.38         | 3.62     | 3.08         | 3.30         |
| G⁺TX⁻G⁺    | 4.03    | 3.41    | 3.88      | 3.46      | 3.77         | 3.38         | 3.62     | 3.07         | 3.29         |
| TG⁺X⁻G⁻    | 3.94    | 3.35    | 3.80      | 3.42      | 3.70         | 3.34         | 3.57     | 3.03         | 3.26         |
| TG⁺X⁻G⁺    | 3.90    | 3.32    | 3.77      | 3.38      | 3.66         | 3.30         | 3.53     | 2.99         | 3.19         |
| G⁺G⁺G⁺X⁻   | 4.62    | 3.56    | 4.36      | 3.64      | 4.19         | 3.52         | 3.99     | 3.11         | 3.54         |
| G⁺G⁺X⁻G⁻   | 4.57    | 3.55    | 4.32      | 3.64      | 4.16         | 3.52         | 3.97     | 3.09         | 3.45         |
| TX⁺G⁻X⁻    | 5.59    | 4.69    | 5.41      | 4.81      | 5.28         | 4.71         | 5.09     | 4.33         | 4.61         |
| G⁺X⁻X⁻G⁺   | 5.92    | 4.98    | 5.70      | 5.06      | 5.54         | 4.95         | 5.32     | 4.53         | 4.78         |
| G⁺X⁺G⁺X⁻   | 6.50    | 5.56    | 6.31      | 5.69      | 6.17         | 5.59         | 5.97     | 5.12         | 5.42         |
| L⁺G⁻X⁻G⁺   | 7.02    | 6.17    | 6.85      | 6.30      | 6.71         | 6.19         | 6.49     | 5.74         | 5.97         |
| X⁺G⁻G⁺X⁻   | 7.10    | 6.22    | 6.98      | 6.40      | 6.86         | 6.32         | 6.68     | 5.92         | 6.28         |

RMS     | 0.76    | 0.10    | 0.59      | 0.15      | 0.48         | 0.08         | 0.34     | 0.24         |
MAD     | 0.69    | 0.08    | 0.54      | 0.13      | 0.44         | 0.06         | 0.31     | 0.23         |
MD      | 1.21    | 0.20    | 0.92      | 0.33      | 0.76         | 0.22         | 0.55     | 0.43         |
Table 4: Dual basis resolution-of-the-identity double hybrid aug-cc-pVTZ conformer energies for the n-heptane conformers in kcal/mol. *Ab initio* reference energies are the MP2:CC values from Gruzman et al. 29

| cc-pVTZ       | B2-PLYP | B2GP-PLYP | DSD-BLYP | DSD-PBEPP86 | *ab initio* |
|---------------|---------|-----------|----------|-------------|-------------|
|               | -D3     | -D3       | -D3      | -D2         |             |
| n-heptane     |         |           |          |             |             |
| TTTT          | 0.00    | 0.00      | 0.00     | 0.00        | 0.00        |
| TTTG^-        | 0.77    | 0.62      | 0.72     | 0.62        | 0.69        |
| TTG^-T        | 0.78    | 0.61      | 0.73     | 0.61        | 0.69        |
| TTG^-G^-      | 1.42    | 0.94      | 1.26     | 0.94        | 1.17        |
| TG^-G^-T      | 1.44    | 0.93      | 1.28     | 0.93        | 1.18        |
| TG^-TG^-      | 1.56    | 1.22      | 1.45     | 1.21        | 1.38        |
| G^-TTG^-      | 1.54    | 1.22      | 1.44     | 1.22        | 1.37        |
| G^-TTG^-      | 1.55    | 1.22      | 1.45     | 1.23        | 1.38        |
| TG^-TG^-      | 1.64    | 1.35      | 1.55     | 1.36        | 1.49        |
| TG^-G^-G^-    | 2.06    | 1.26      | 1.80     | 1.26        | 1.65        |
| G^-TG^-G^-    | 2.18    | 1.49      | 1.96     | 1.50        | 1.82        |
| G^-TG^-G^-    | 2.27    | 1.68      | 2.08     | 1.69        | 1.97        |
| G^-G^-G^-G^-  | 2.69    | 1.63      | 2.35     | 1.63        | 2.15        |
| TTX^-G^-      | 3.11    | 2.65      | 3.00     | 2.70        | 2.92        |
| TTTG^-X^+     | 3.16    | 2.72      | 3.07     | 2.77        | 2.98        |
| TG^-X^-T      | 3.05    | 2.58      | 2.94     | 2.62        | 2.85        |
| TG^-G^-X^-    | 3.82    | 2.96      | 3.61     | 3.02        | 3.45        |
| TX^-G^-G^-    | 3.71    | 2.91      | 3.52     | 2.97        | 3.37        |
| G^-TX^-G^-    | 3.91    | 3.26      | 3.75     | 3.33        | 3.63        |
| G^-TG^-X^-    | 3.96    | 3.36      | 3.81     | 3.41        | 3.70        |
| G^-TX^-G^-    | 3.98    | 3.36      | 3.82     | 3.40        | 3.70        |
| TG^-X^-G^-    | 3.89    | 3.31      | 3.75     | 3.36        | 3.63        |
| TG^-X^-G^-    | 3.86    | 3.28      | 3.72     | 3.33        | 3.60        |
| G^-G^-G^-X^-  | 4.54    | 3.49      | 4.27     | 3.56        | 4.08        |
| G^-G^-X^-G^-  | 4.49    | 3.48      | 4.23     | 3.55        | 4.05        |
| TX^-G^-X^-    | 5.50    | 4.60      | 5.31     | 4.71        | 5.16        |
| G^-X^-X^-G^-  | 5.82    | 4.89      | 5.59     | 4.96        | 5.41        |
| G^-X^-G^-X^-  | 6.42    | 5.48      | 6.22     | 5.60        | 6.05        |
| L^-G^-X^-G^-  | 6.93    | 6.07      | 6.74     | 6.18        | 6.57        |
| X^-G^-G^-X^-  | 7.06    | 6.17      | 6.92     | 6.34        | 6.77        |
| RMS           | 0.71    | 0.06      | 0.53     | 0.09        | 0.41        |
| MAD           | 0.65    | 0.05      | 0.49     | 0.08        | 0.37        |
| MD            | 1.14    | 0.11      | 0.81     | 0.21        | 0.63        |
Table 5: Dual basis resolution-of-the-identity double hybrid aug-cc-pVTZ conformer energies for the S22 test set of non-covalent bonded molecules in kcal/mol. *Ab initio* reference energies are the CBS(Δa(DT)Z) values from Takatani *et al.*30

|                        | cc-pVTZ | B2-PLYP | B2GP-PLYP | DSD-BLYP | DSD-PBEP86 | *ab initio* |
|------------------------|---------|---------|-----------|----------|------------|-------------|
|                        | −D3     | −D3     | −D3       | −D2      |            |             |
| **H-bonded complexes** |         |         |           |          |            |             |
| (NH₃)₂                 | -2.58   | -3.06   | -2.72     | -3.05    | -2.73      | -3.04       | -2.85 | -3.23 | -3.17 |
| (H₂O)₂                | -4.64   | -5.03   | -4.78     | -5.05    | -4.73      | -4.99       | -4.73 | -4.95 | -5.02 |
| Formic acid dimer      | -17.52  | -18.76  | -17.92    | -18.80   | -17.71     | -18.53      | -17.61 | -18.31 | -18.80 |
| Formamide dimer        | -14.34  | -15.70  | -14.72    | -15.68   | -14.61     | -15.50      | -14.62 | -15.35 | -16.12 |
| Uracil dimer           | -18.46  | -20.23  | -18.96    | -20.21   | -18.84     | -20.01      | -18.66 | -19.58 | -20.69 |
| 2-Pyridoxine -         |         |         |           |          |            |             |
| 2-Aminopyridine        | -14.84  | -16.89  | -15.30    | -16.73   | -15.34     | -16.67      | -15.38 | -16.48 | -17.00 |
| Adenine-thymine WC     | -13.95  | -16.16  | -14.45    | -16.02   | -14.49     | -15.94      | -14.58 | -15.75 | -16.74 |
| **Dispersion dominated complexes** |         |         |           |          |            |             |
| (CH₄)₂                 | 0.08    | -0.33   | -0.03     | -0.30    | -0.07      | -0.32       | -0.21  | -0.44 | -0.53 |
| (C₂H₄)₂               | -0.22   | -1.35   | -0.49     | -1.30    | -0.57      | -1.32       | -0.82  | -1.41 | -1.50 |
| Benzene-CH₄           | -0.09   | -1.28   | -0.39     | -1.20    | -0.52      | -1.28       | -0.77  | -1.38 | -1.45 |
| PD benzene dimer       | 1.05    | -1.99   | 0.20      | -1.83    | -0.30      | -2.20       | -0.81  | -2.39 | -2.62 |
| Pyrazine dimer         | -0.39   | -3.56   | -1.31     | -3.46    | -1.83      | -3.83       | -2.28  | -3.99 | -4.20 |
| Uracil dimer stack     | -4.29   | -8.91   | -5.40     | -8.54    | -5.87      | -8.79       | -6.32  | -8.81 | -9.74 |
| Idole-benzene stack    | 0.66    | -3.68   | -0.57     | -3.50    | -1.31      | -4.04       | -1.93  | -4.28 | -4.59 |
| Adenine-thymine stack  | -4.03   | -10.40  | -5.74     | -10.09   | -6.57      | -10.63      | -7.24  | -10.88 | -11.66 |
| **Mixed complexes**    |         |         |           |          |            |             |
| Ethene-ethine          | -1.00   | -1.55   | -1.14     | -1.51    | -1.17      | -1.51       | -1.29  | -1.56 | -1.51 |
| Benzene-H₂O            | -1.92   | -3.09   | -2.22     | -3.02    | -2.31      | -3.05       | -2.51  | -3.16 | -3.29 |
| Benzene-NH₃           | -0.91   | -2.12   | -1.22     | -2.03    | -1.33      | -2.09       | -1.56  | -2.19 | -2.32 |
| Benzene-NCN            | -3.11   | -4.61   | -3.55     | -4.59    | -3.66      | -4.63       | -3.90  | -4.76 | -4.55 |
| Benzene dimer T        | -0.56   | -2.50   | -1.06     | -2.39    | -1.30      | -2.54       | -1.61  | -2.62 | -2.71 |
| Indole-benzene T       | -2.75   | -5.31   | -3.47     | -5.21    | -3.80      | -5.42       | -4.18  | -5.64 | -5.62 |
| Phenol dimer           | -4.54   | -6.79   | -5.12     | -6.69    | -5.31      | -6.77       | -5.48  | -6.61 | -7.09 |
| RMS                    | 2.98    | 0.48    | 2.31      | 0.60     | 2.03       | 0.46        | 1.77   | 0.49 | 0.49 |
| MAD                    | 2.39    | 0.36    | 1.84      | 0.45     | 1.66       | 0.36        | 1.44   | 0.36 | 0.36 |
| MD                     | 7.63    | 1.26    | 5.92      | 1.57     | 5.09       | 1.03        | 4.42   | 1.11 | 1.11 |
Table 6: Dual basis resolution-of-the-identity double hybrid aug-cc-pVTZ conformer energies for the S22 test set of non-covalent bonded molecules in kcal/mol. \textit{Ab initio} reference energies are the CBS($\Delta a(DTZ)$) values from Takatani \textit{et al.}\textsuperscript{30}

|              | aug-cc-pVTZ | B2-PLYP | B2GP-PLYP | DSD-BLYP | DSD-PBEP86 | \textit{ab initio} |
|--------------|-------------|---------|-----------|----------|------------|-------------------|
|              | $-D_3$      | $-D_3$  | $-D_3$    | $-D_3$   | $-D_2$     |                   |
| **H-bonded complexes** |             |         |           |          |            |                   |
| (NH$_3$)$_2$ | -2.58       | -3.06   | -2.75     | -3.08    | -2.79      | -2.90             |
| (H$_2$O)$_2$ | -4.68       | -5.07   | -4.82     | -5.09    | -4.80      | -4.81             |
| Formic acid dimer | -17.67     | -18.90  | -18.14    | -19.03   | -17.99     | -18.81            |
| Formamide dimer | -14.60     | -15.97  | -15.06    | -16.02   | -15.01     | -15.74            |
| Uracil dimer  | -18.82      | -20.59  | -19.38    | -20.63   | -19.33     | -19.13            |
| 2-pyridoxine - |                   |         |           |          |            |                   |
| 2-aminopyridine | -15.07     | -17.11  | -15.60    | -17.03   | -15.70     | -15.74            |
| Adenine thymine WC | -14.27     | -16.48  | -14.85    | -16.42   | -14.95     | -15.04            |
| **Dispersion dominated complexes** |             |         |           |          |            |                   |
| (CH$_4$)$_2$ | 0.03        | -0.38   | -0.09     | -0.36    | -0.14      | -0.28             |
| (C$_2$H$_4$)$_2$ | -0.32      | -1.44   | -0.61     | -1.42    | -0.72      | -0.97             |
| Benzene-CH$_4$ | -0.17       | -1.36   | -0.50     | -1.31    | -0.65      | -0.90             |
| PD Benzene dimer | 0.71       | -2.33   | -0.21     | -2.25    | -0.78      | -1.28             |
| Pyrazine dimer | -0.79       | -3.96   | -1.80     | -3.95    | -2.40      | -2.84             |
| Uracil dimer stack | -4.84      | -9.47   | -6.09     | -9.23    | -6.66      | -7.11             |
| Indole-benzene stack | 0.19      | -4.15   | -1.15     | -4.08    | -1.97      | -2.58             |
| Adenine-thymine stack | -4.75      | -11.12  | -6.62     | -10.97   | -7.59      | -8.24             |
| **Mixed complexes** |             |         |           |          |            |                   |
| Ethene-ethine | -1.02       | -1.57   | -1.18     | -1.54    | -1.22      | -1.57             |
| Benzene-H$_2$O | -2.07       | -3.23   | -2.41     | -3.20    | -2.53      | -3.27             |
| Benzene-NH$_3$ | -1.04       | -2.25   | -1.38     | -2.19    | -1.53      | -2.28             |
| Benzene-HCN   | -3.14       | -4.63   | -3.61     | -4.66    | -3.76      | -4.73             |
| Benzene dimer T | -0.68       | -2.62   | -1.23     | -2.56    | -1.51      | -2.75             |
| Indole-benzene T | -2.87      | -5.42   | -3.65     | -5.39    | -4.03      | -5.66             |
| Phenol dimer  | -4.73       | -6.98   | -5.37     | -6.94    | -5.61      | -7.08             |

|              | RMS         | MAD     | MD        |          |            |                   |
|--------------|-------------|---------|-----------|----------|------------|-------------------|
|              | 2.70        | 0.21    | 1.96      | 0.27     | 1.62       | 0.13              |
|              | 2.17        | 0.16    | 1.56      | 0.20     | 1.33       | 0.09              |
|              | 6.91        | 0.54    | 5.04      | 0.69     | 4.07       | 0.34              |