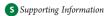# Obtaining Good Performance With Triple-ζ-Type Basis Sets in Double-Hybrid Density Functional Theory Procedures

Bun Chan* and Leo Radom*

School of Chemistry and ARC Center of Excellence for Free Radical Chemistry and Biotechnology, University of Sydney, Sydney, NSW 2006, Australia

S *Supporting Information*

ABSTRACT: A variety of combinations of B-LYP-based double-hybrid density functional theory (DHDFT) procedures and basis sets have been examined. A general observation is that the optimal combination of exchange contributions is in the proximity of 30% Becke 1988 (B88) exchange and 70% Hartree−Fock (HF) exchange, while for the correlation contributions, the use of independently optimized spin-component-scaled Møller−Plesset second-order perturbation theory (SCS-MP2) parameters (MP2OS and MP2SS) is beneficial. The triple-ζ Dunning aug′-cc-pVTZ+d and Pople 6-311+G(3df,2p)+d basis sets are found to be cost-effective for DHDFT methods. As a result, we have formulated the DuT-D3 DHDFT procedure, which employs the aug′-cc-pVTZ+d basis set and includes 30% B88 and 70% HF exchange energies, 59% LYP, 47% MP2OS, and 36% MP2SS correlation energies, and a D3 dispersion correction with the parameters $s_6 = 0.5$, $s_{r,6} = 1.569$, and $s_8 = 0.35$. Likewise, the PoT-D3 DHDFT procedure was formulated with the 6-311+G(3df,2p)+d basis set and has 32% B88 and 68% HF exchange energies, 63% LYP, 46% MP2OS, and 27% MP2SS correlation energies, and the D3 parameters $s_6 = 0.5$, $s_{r,6} = 1.569$, and $s_8 = 0.30$. Testing using the large E3 set of 740 energies demonstrates the robustness of these methods. Further comparisons show that the performance of these methods, particularly DuT-D3, compares favorably with the previously reported DSD-B-LYP and DSD-B-LYP-D3 methods used in conjunction with quadruple-ζ aug′-pc3+d and aug′-def2-QZVP basis sets but at lower computational expense. The previously reported ωB97X-(LP)/6-311++G(3df,3pd) procedure also performs very well. Our findings highlight the cost-effectiveness of appropriate- and moderate-sized triple-ζ basis sets in the application of DHDFT procedures.

INTRODUCTION

The appearance of the B2-PLYP method[1] has sparked considerable interest in the further development of double-hybrid density functional theory (DHDFT) procedures[2−13] due to their superior performance when compared with conventional DFT methods.[12,14] The DHDFT procedures contain wave function-type components, namely Hartree−Fock exchange and Møller−Plesset second-order perturbation theory (MP2) correlation. For instance, the energy given by B2-PLYP is evaluated with exchange energies from Becke 1988 (B88, E_X^{B88}) and Hartree−Fock (HF, E_X^{HF}) and correlation energies from Lee−Yang−Parr (LYP, E_C^{LYP}) and MP2 (E_C^{MP2}), according to eq 1:

$$E_{B2\text{-}PLYP} = c_{B88}E_X^{B88} + c_{HF}E_X^{HF} + c_{LYP}E_C^{LYP} + c_{MP2}E_C^{MP2} \quad (1)$$

The coefficients for the various components were determined[1] by fitting to the heats of formation in the G2/97 training set,[15] with the conditions $c_{B88} + c_{HF} = 1$ and $c_{LYP} + c_{MP2} = 1$. The values recommended for B2-PLYP are $c_{B88} = 0.47$, $c_{HF} = 0.53$, $c_{LYP} = 0.73$, and $c_{MP2} = 0.27$. A variety of DHDFT procedures have been subsequently developed with the aim of further improving the accuracy and the versatility.[2−12] These include the recently reported DSD-B-LYP procedure.[11] It makes use of the spin-component-scaled MP2 (SCS-MP2)[16] methodology, in which opposite-spin (MP2OS) and same-spin (MP2SS) contributions to the MP2 correlation energy are treated separately and includes an empirical correction (E_D)[17] for

dispersion interactions:

$$E_{DSD\text{-}B\text{-}LYP} = c_{B88}E_X^{B88} + c_{HF}E_X^{HF} + c_{LYP}E_C^{LYP} + c_{OS}E_C^{MP2OS} + c_{SS}E_C^{MP2SS} + E_D \quad (2)$$

The five scaling coefficients and the parameter in E_D in eq 2 were obtained, with the condition $c_{B88} + c_{HF} = 1$, by fitting to a collection of six training sets, comprising atomization energies (W4/08),[4] main-group reaction barriers (DBH24),[18] weak interactions (S22),[19] artificially generated species (MB08)[20] and transition-metal chemistry (Pd[21] and Grubbs).[22] We will refer to this collection as the DSD set hereafter. The recommended scaling coefficients for DSD-B-LYP are $c_{B88} = 0.31$, $c_{B88} = 0.69$, $c_{LYP} = 0.54$, $c_{OS} = 0.46$, and $c_{SS} = 0.37$. Recently, a slightly modified DSD-B-LYP method (DSD-B-LYP-D3)[12] has been shown to perform well on the diverse and sizable GMTKN30 test set.[12] This variant uses the D3 scheme[23] for the dispersion term.

The optimized parameters for DHDFT methods have often been obtained using quadruple-ζ basis sets of different styles. For instance, the coefficients for the original B2-PLYP[1] were obtained in combination with QZV3P, which is a modified first-generation Ahlrichs basis set.[24] The variants B2T-PLYP,[3] B2K-PLYP,[3] and B2GP-PLYP[4] were derived mainly from a quadruple-ζ polarization-consistent (Jensen) basis set,[25] namely aug-pc3. A correlation-consistent (Dunning) basis set,[26] cc-pVQZ, was used

for ROB2-PLYP.[7] The ωB97X-2 procedure[6] was developed with the complete-basis-set limit using triple- and quadruple-ζ Dunning sets for extrapolation. A mixture of aug′-pc3 (aug′ denotes the inclusion of diffuse functions on nonhydrogen atoms) and second-generation Ahlrichs basis sets,[27] def2-QZVP and def2-QZVPP, were the major basis sets employed for the development of DSD-B-LYP.[11] The recently proposed PTPSS[12] and PW-PB95[12] procedures were optimized mainly with the def2-QZVP basis set. Nonetheless, smaller triple-ζ basis sets have also been employed for the development of DHDFT procedures, but the resulting procedures show variable performance. Thus, the B2−P3LYP method[5] was optimized for cc-pVTZ, and this combination leads to a mean absolute deviation (MAD) from benchmark values of 13.0 kJ mol^{-1} for the G2/97 set of atomization energies.[15] The Pople basis set 6-311+G(3df,2p)[28] was employed in deriving XYG3,[8] and it has an MAD of 7.6 kJ mol^{-1} for the G3/99 set of heats of formation (ΔH_f).[29] In addition, the ωB97X-2(LP) procedure[6] was parametrized with the 6-311++G(3df,3pd) basis set and yields a very impressive MAD of 6.4 kJ mol^{-1} for G3/99 ΔH_f.

The large variety of mostly quadruple-ζ basis sets employed in the development of DHDFT procedures begs the following questions: (1) Is a quadruple-ζ basis set required for good performance, or can one utilize more manageable triple-ζ basis sets without significantly sacrificing accuracy? (2) Do basis sets of similar size but of different types give comparable results, or is one type of basis set particularly suitable for DHDFT methods?

Goerigk and Grimme have attempted to answer the first question by testing a variety of DHDFT procedures on the GMTKN30 set with the (aug-)def2-TZVPP and (aug-)def2-QZVP basis sets.[12] They find that, for the PW-PB95-D3 procedure for which the basis set dependence is the smallest, the MAD from benchmark values for the triple-ζ basis set is greater than that for the quadruple-ζ basis set by 0.2 kcal mol^{-1} (~0.8 kJ mol^{-1}).[30] Because DHDFT contains exchange and correlation components from both DFT and wave function methods, the second question is particularly interesting. Does DHDFT work better with the Jensen basis sets, which are designed for DFT procedures, or with the Dunning sets that are tailored for wave function correlation methods? How about the performance of the Ahlrichs sets that are often used in the development of DHDFT or the popular Pople basis sets?

The aim of the present study is to address these questions. We also attempt to identify other important components of the calculations that contribute to the good performance of DHDFT procedures and features that would broaden their applicability. In particular, we strive to identify triple-ζ basis sets that yield results of comparable quality to the larger quadruple-ζ basis sets, thus reducing the computational cost for performing DHDFT calculations and enabling their use in situations where the use of a quadruple-ζ basis set is computationally too demanding.

■ COMPUTATIONAL DETAILS

Standard wave function and DFT calculations[31] were carried out with Gaussian 03[32] and Gaussian 09.[33] D3 dispersion corrections were obtained with the dftd3 program.[23] Unless otherwise noted, geometries were optimized using BMK[34] with the 6-31+G(2df,p) basis set. This level of theory has previously been shown to represent a cost-effective means for obtaining reliable geometries.[35] Energies at 0 K incorporate zero-point vibrational energies, obtained with scaled (0.9770) BMK/6-31+G(2df,p)

frequencies, while 298 K enthalpies additionally include thermal corrections derived from frequencies scaled by 0.9627.[35,36]

While more detailed descriptions of the various basis sets employed in the present study will be given within the main text, for convenience we provide a brief summary here. For the sake of simplicity, in the tables we abbreviate the Dunning basis sets cc-pVnZ as VnZ, and the aug-cc-pVnZ basis sets as AVnZ, where n = T and Q. The use of ′ in a basis set, for example, in aug′-cc-pVTZ+d and def2-TZVPD′+d, indicates the use of diffuse functions only on nonhydrogen atoms. The aug′-def2-TZVP basis set represents the def2-TZVP basis set augmented with diffuse functions taken from aug′-cc-pVTZ. We have also employed the aug′-def2-QZVP basis set, in which diffuse functions from aug′-cc-pVQZ are added to the def2-QZVP basis set. Our baseline basis set for the purpose of comparison is the Dunning (aug-)cc-pVTZ basis set, in which (aug-) denotes the inclusion of diffuse functions only for the calculation of electron affinities. The corresponding selectively augmented triple-ζ Pople, Ahlrichs, and Jensen basis sets are denoted 6-311(++)G(3df,2p), def2-TZVP(D), and (aug-)pc2, respectively. They are derived from the combinations 6-311G(3df,2p)/6-311++G(3df,2p), def2-TZVP/def2-TZVPD,[37] and pc2/aug-pc2.

Basis sets that are external to the Gaussian 03 and 09 programs were obtained from the Environmental Molecular Sciences Laboratory (EMSL) basis set library.[38] The inclusion of tight d functions for the elements Al−Ar is indicated by the suffix +d, as, for example, in aug′-cc-pVTZ+d and 6-311+G(3df,2p)+d. We derived the tight d functions for use in the aug′-pc2+d and aug′-pc3+d basis sets according to the recommendation by Martin.[39] Thus, the exponents were obtained by scaling the existing largest d exponents by 2.5. We also employ the same approach for obtaining tight d functions for use in the def2-TZVPD′+d, aug′-def2-TZVP+d, and 6-311+G(3df,2p)+d basis sets.

The frozen-core approximation is employed in the evaluation of the MP2 correlation energy, unless otherwise noted. Parameters for the quantum mechanical DHDFT procedures that were reoptimized in the present study were obtained by fitting to the G2/97 training set, while the parameters for the empirical D3 dispersion correction were determined by adjustment for the larger E3 set, as we find that this is necessary in order to provide further robustness for a more diverse range of systems. Following previous practice,[35] our optimization procedures involved minimizing the average of the mean absolute deviation (MAD) from benchmark values and the standard deviation (SD) of these deviations. All relative energies are reported in kJ mol^{-1}.

■ RESULTS AND DISCUSSION

In the present study, we focus on the B-LYP functional as the DFT component, as this is by far the most commonly employed functional in DHDFT procedures.[1,3−5,7−11] For most of the study, we examine three forms of DHDFT methods: (1) B2-PLYP-type procedures where the DHDFT energy is derived from eq 1 and satisfies the conditions $c_{B88} + c_{HF} = 1$ and $c_{LYP} + c_{MP2} = 1$. Included in this category are B2-PLYP, B2T-PLYP, B2GP-PLYP, and B2K-PLYP, which offer increasing wave function contributions to the DHDFT energy in the above order. We term such procedures STD-DHDFT, where STD denotes "standard"; (2) DHDFT procedures that are similar to B2-PLYP but with c_{MP2} reoptimized independently of the default value of c_{LYP}, which means that $c_{LYP} + c_{MP2}$ is no longer constrained to be equal to 1. We term such procedures UCMP-DHDFT, where UCMP

Table 1. MADs From Experimental Values (kJ mol^{-1}) for Various DHDFT Procedures with a Variety of Basis Sets for the G2/97 Set and its Subsets

	1	2	3	4	5	6	7	8	9	10	11	12
DHDFT	B2-PLYP	B2-PLYP^c	B2-PLYP	B2-PLYP	B2-PLYP	B2-PLYP	B2-PLYP	B2-PLYP	B2-PLYP	B2T-PLYP	B2GP-PLYP	B2K-PLYP
basis set^a	(A)VTZ	(A)VTZ	(A)VTZ+d	(A)VQZ	AVTZ	A′VTZ	6-311(++)G(3df,2p)	def2-TZVP(D)	(aug-)pc2	(A)VTZ	(A)VTZ	(A)VTZ
						STD-DHDFT							
G2/97^b	16.7	12.6	15.2	9.8	14.3	14.7	14.3	20.4	13.4	19.9	19.8	22.3
ΔH_f	22.2	14.1	19.4	10.2	19.0	19.7	16.1	27.4	16.3	28.9	29.5	34.5
IE	14.9	14.6	14.9	11.9	11.8	11.9	15.9	14.3	13.5	13.9	12.9	12.2
EA	7.1	7.0	6.7	6.5	7.1	7.3	8.3	14.1	7.1	8.0	7.9	8.7
PA	4.8	4.7	4.2	3.7	5.9	6.0	7.3	4.2	3.4	5.0	5.2	5.6
						UCMP-DHDFT^d							
G2/97	10.2	10.2	9.1	8.7	9.2	9.3	12.0	11.7	9.3	9.0	8.7	8.7
ΔH_f	10.4	10.1	8.4	8.4	9.6	9.8	13.0	12.4	9.0	9.0	8.8	9.1
IE	12.4	13.3	12.6	11.2	10.3	10.3	14.2	11.3	12.1	10.9	10.1	9.1
EA	6.9	6.5	6.4	6.4	6.7	6.8	6.9	11.6	6.7	6.8	7.0	7.4
PA	4.7	4.6	3.9	3.8	6.4	6.5	7.2	4.6	3.5	4.8	4.8	5.0
						SCS-DHDFT^e							
G2/97	10.1	10.2	9.0	8.7	9.1	9.2	11.1	10.8	9.3	9.0	8.7	8.5
ΔH_f	10.3	10.1	8.1	8.4	9.6	9.7	11.0	10.6	9.0	8.9	8.8	8.9
IE	12.5	13.3	12.6	11.2	10.2	10.2	14.5	11.3	12.0	10.9	10.1	9.1
EA	6.7	6.4	6.3	6.3	6.6	6.7	6.9	11.5	6.6	6.8	6.8	7.2
PA	4.5	4.6	3.9	3.6	6.1	6.2	6.7	3.5	3.4	4.7	4.7	5.0
timing^f	1.0	1.1	1.0	12.1	4.6	2.8	0.9	0.6	1.0	1.0	1.0	1.0

^{a} (A), (++), (D) and (aug-) indicate inclusion of diffuse functions only for the calculation of electron affinities, VnZ = cc-pVnZ, AVnZ = aug-cc-pVnZ, A′VnZ = VnZ for hydrogen and AVnZ for other elements. ^{b} ΔH_f = heat of formation (298 K), IE = ionization energy (0 K), EA = electron affinity (0 K), and PA = proton affinity (0 K). ^{c} All electrons are correlated for the MP2 treatment. ^{d} Each c_{MP2} parameter is optimized for the specific procedure and basis set. ^{e} The c_{OS} and c_{SS} parameters are optimized for each method. ^{f} Relative to the total time for B2-PLYP/(A)VTZ calculations for the G2/97 set.

signifies "unconstrained MP2 correlation"; and (3) DSD-B-LYP-like procedures[11] in which the energy is given by eq 2 with c_{OS} and c_{SS} optimized but without the D correction. We term such procedures SCS-DHDFT. While we will examine the effect of dispersion corrections at a later stage, we attempt initially to recover the maximum amount of long-range effects using quantum mechanics and employ the dispersion correction to provide further improvement to the procedure.

Important Components for DHDFT Procedures. In this section, we use frozen-core B2-PLYP/(aug-)cc-pVTZ as our baseline method to examine a variety of options for improving the performance. The (aug-)cc-pVTZ basis set includes diffuse functions only for the evaluation of electron affinities (EAs), which we deem a minimal requirement for obtaining reliable energies. The MADs for the G2/97 set and its subsets are given in Table 1.

We first note that, regardless of the basis set used, the MADs for the three different types of DHDFT procedures generally decrease in the order STD-DHDFT > UCMP-DHDFT ∼ SCS-DHDFT. In particular, STD-DHDFT generally yields significantly poorer performance for ΔH_f than is obtained for the corresponding UCMP-DHDFT and SCS-DHDFT procedures. We have examined the values of the reoptimized c_{MP2} parameters in the UCMP-DHDFT procedures (Supporting Information, Table S1) and find that they are all larger than their originally

recommended values. In other words, the imposed constraint of $c_{LYP} + c_{MP2} = 1$ in the original B2-PLYP formalism appears to lead to insufficient incorporation of electron correlation. Grimme has suggested that the inclusion of a relatively large amount of nonlocal correlation is the major contributing factor for the good performance of the XYG3 procedure.[12] Our finding of an optimal correlation energy in excess of $c_{LYP} + c_{MP2} = 1$ is consistent with such a proposition. It is also noteworthy that the added flexibility in the SCS-DHDFT scheme does not lead to a significant improvement over UCMP-DHDFT in most cases.

We now examine the various options for improving frozen-core B2-PLYP, UCMP-B2-PLYP, and SCS-B2-PLYP with the (aug-)cc-pVTZ basis set for which the MADs are 16.7, 10.2, and 10.1 kJ mol^{-1}, respectively (Table 1, column 1). We find that, while correlating all electrons for MP2 (column 2) appears to be beneficial for B2-PLYP, it provides little improvement for UCMP-B2-PLYP and SCS-B2-PLYP. On the other hand, the inclusion of tight d functions for second-row atoms leads to somewhat lower overall MADs for all three variants of B2-PLYP (column 3). When the quadruple-ζ basis set is used (column 4), the MADs are all lowered substantially, with values of ∼8.5−10 kJ mol^{-1} for the overall G2/97 set. A small overall improvement is also achieved when one includes diffuse functions for the calculation of heats of formation, ionization energies (IEs), and proton affinities (PAs) as well as for electron affinities (EAs)

Table 2. MADs from Experimental Values (kJ mol^{-1}) for the G2/97 Set and its Subsets for B2-PLYP-Type and B2K-PLYP-Type Procedures with a Variety of Basis Sets[a]

DHDFT	1	2	3	4	5	6	7	8	9	10
	B2-PLYP	B2-PLYP	B2-PLYP	B2-PLYP	B2-PLYP	B2K-PLYP	B2K-PLYP	B2K-PLYP	B2K-PLYP	B2K-PLYP
basis set	def2-TZVPD′+d	6-311+G(3df,2p)+d	aug′-pc2+d	aug′-def2-TZVP+d	A′VTZ+d	def2-TZVPD′+d	6-311+G(3df,2p)+d	aug′-pc2+d	aug′-def2-TZVP+d	A′VTZ+d
					STD-DHDFT					
G2/97	19.6	13.8	11.5	16.3	13.3	26.0	18.5	14.9	21.9	17.6
ΔH_f	25.6	17.1	13.1	22.8	17.0	39.3	27.2	20.6	34.7	26.7
IE	12.9	12.4	12.2	12.2	11.8	10.9	10.2	10.1	10.1	9.5
EA	16.2	8.7	7.2	7.2	7.0	17.8	10.4	9.1	8.9	8.5
PA	6.4	5.8	4.8	7.2	5.2	6.5	5.8	4.8	7.2	5.2
					UCMP-DHDFT[b]					
G2/97	11.5	10.1	8.9	10.0	8.4	10.4	8.8	7.5	9.2	6.6
ΔH_f	11.8	11.0	8.6	11.4	8.1	10.8	9.6	7.0	10.9	5.7
IE	10.3	10.9	11.2	10.1	10.3	8.1	8.4	8.6	8.0	7.9
EA	13.4	6.9	6.8	6.5	6.3	13.7	7.9	7.6	7.2	7.0
PA	7.2	6.3	5.0	7.9	5.7	7.0	6.2	5.0	7.8	5.5
					SCS-DHDFT[c]					
G2/97	10.8	9.5	8.7	9.2	8.3	8.4	7.5	7.2	6.8	6.1
ΔH_f	10.4	10.0	8.3	9.9	8.1	6.6	7.0	6.4	6.3	5.0
IE	10.2	10.9	11.2	10.0	10.2	7.9	8.3	8.6	7.8	7.7
EA	13.5	6.7	6.6	6.3	6.3	13.9	8.0	7.4	6.7	6.7
PA	5.7	4.9	4.4	6.3	5.1	5.5	4.8	4.4	6.2	4.9
timing[d]	1.0	1.1	2.9	2.0	2.8	1.0	1.2	3.0	2.0	2.8

[a] Augmented in each case with diffuse functions for heavy atoms and tight d functions for second-row group 13−18 elements. [b] Each c_{MP2} parameter is optimized for the specific procedure and basis set. [c] The c_{OS} and c_{SS} parameters are optimized for each method. [d] Relative to the total time for B2-PLYP/(A)VTZ calculations for the G2/97 set.

(column 5). Thus, the MADs for the G2/97 set for B2-PLYP, UCMP-B2-PLYP and SCS-B2-PLYP, with aug-cc-pVTZ, are 14.3, 9.2, and 9.1 kJ mol^{-1}, respectively. The lowering of the MADs for ΔH_f and IEs is small but significant, while the performance for PAs is slightly worse. We find that exclusion of diffuse functions on hydrogen atoms from the aug-cc-pVTZ basis set, i.e., aug′-cc-pVTZ (column 6), does not lead to a significant deterioration of performance.

Turning our attention to timing comparisons (Table 1), we find that, for the G2/97 set, the use of all electrons for the MP2 correlation treatment (column 2) and the inclusion of tight d functions (column 3) does not significantly affect the timings when compared with frozen-core (aug-)cc-pVTZ (column 1). Increasing the basis set size to (aug-)cc-pVQZ (column 4) is significantly more expensive (12.1×). The use of the aug-cc-pVTZ basis set (column 5) leads to a less substantial increase in timing (4.6×), while the omission of diffuse functions for hydrogen in aug′-cc-pVTZ (column 6) further reduces the time required (2.8×). Given that (aug-)cc-pVQZ, aug-cc-pVTZ, and aug′-cc-pVTZ basis sets lead to similar results for UCMP-B2-PLYP and SCS-B2-PLYP, we consider the use of aug′-cc-pVTZ a more cost-effective means for improving the performance than (aug-)cc-pVQZ. We also deem the inclusion of tight d functions cost-effective, as it leads to a small but noticeable improvement in performance, with minimal increase in computational cost.

We next examine the performance of four different families of partially augmented triple-ζ basis sets (columns 1 and 7−9) used in conjunction with the three types of DHDFT procedures, namely B2-PLYP, UCMP-B2-PLYP, and SCS-B2-PLYP (Table 1). These basis sets include diffuse functions only for the calculation of EAs. We can see that 6-311(++)G(3df,2p) (column 7) performs somewhat better than (aug-)cc-pVTZ for B2-PLYP but does slightly less well for UCMP-B2-PLYP and SCS-B2-PLYP. The partially augmented Ahlrichs set def2-TZVP(D) (column 8) comprises the def2-TZVP basis set for neutral molecules and cations and the recently developed def2-TZVPD basis set for anions,[37] in which a small set of diffuse functions is added, and they are optimized for the calculation of polarizability. The use of the def2-TZVP(D) basis set yields larger MADs for B2-PLYP when compared with (aug-)cc-pVTZ. Its performance versus the Dunning (aug-)cc-pVTZ set appears to be only slightly worse when combined with UCMP-B2-PLYP and SCS-B2-PLYP. The use of the Jensen set (aug-)pc2 (column 9) gives MADs that are lower than those for (aug-)cc-pVTZ, regardless of the type of DHDFT procedure employed. We also note that the (aug-)pc2 basis set yields MADs that are not too different from those obtained with aug-cc-pVTZ (column 5) and aug′-cc-pVTZ (column 6).

We now examine the effect of the amount of wave function contribution on the performance of the DHDFT procedures with the (aug-)cc-pVTZ basis set (Table 1, columns 1 and 10−12).

We find that, for STD-DHDFT-type procedures, the overall MADs for the G2/97 set increase in the order B2-PLYP (column 1) < B2T-PLYP (column 10) ∼ B2GP-PLYP (column 11) < B2K-PLYP (column 12), i.e., the MADs increase as the wave function fraction becomes larger. This is mainly associated with the variation in the performance for ΔH_f. For UCMP-DHDFT and SCS-DHDFT, however, the MADs decrease slightly with increasing wave function contribution.

Favorable Combinations of DHDFT Procedures and Basis Sets. While the results presented in Table 1 have provided a useful indication of the variation in the performance of a DHDFT procedure with respect to its form and the basis set employed, the most favorable combination is not yet clear. In search of the optimal and most cost-effective combination of a DHDFT procedure with a specific basis set, we have further examined B2-PLYP- and B2K-PLYP-type procedures combined with the four families of triple-ζ basis sets, in each case augmented with diffuse functions for nonhydrogen atoms and with tight d functions for second-row group 13−18 elements.

We choose B2-PLYP and B2K-PLYP as they represent the two extremes of the DHDFT methods considered, with the former having the smallest and the latter having the largest wave function contributions. For the Ahlrichs def2-TZVP basis set, we have considered two types of diffuse augmentation: (1) the def2-TZVPD′ basis set, which makes use of the def2-TZVPD diffuse functions on nonhydrogen atoms; and (2) the aug′-def2-TZVP basis set, where diffuse functions are taken from the Dunning aug′-cc-pVTZ set. The MADs for the G2/97 set for these combinations are shown in Table 2.

A comparison between Tables 1 (columns 1 and 7−9) and 2 (columns 1−5) shows that the inclusion of additional diffuse functions and tight d functions leads to somewhat lower MADs for the B2-PLYP, UCMP-B2-PLYP, and SCS-B2-PLYP procedures, with small but noticeable improvements for ΔH_f and IE found in most cases. We again find that the MADs decrease in the order STD-DHDFT > UCMP-DHDFT ∼ SCS-DHDFT, which is similar to the trends in Table 1. We also see that the performance of STD-DHDFT for ΔH_f is significantly poorer than those of the corresponding UCMP-DHDFT and SCS-DHDFT procedures. We note that the slightly lower MADs for SCS-DHDFT compared with UCMP-DHDFT are somewhat more obvious in these cases.

We now compare the performance of the different basis sets. It can be seen that, for the STD-DHDFT procedures B2-PLYP (columns 1−5) and B2K-PLYP (columns 6−10), the MADs decrease in the order def2-TZVPD′+d (columns 1 and 6) > aug′-def2-TZVP+d (columns 4 and 9) > 6-311+G(3df,2p)+d (columns 2 and 7) > aug′-cc-pVTZ+d (columns 5 and 10) > aug′-pc2+d (columns 3 and 8). Thus, while (aug-)cc-pVTZ performs less well than the 6-311(++)G(3df,2p) basis set (Table 1, columns 1 and 7), the inclusion of extra functions in the aug′-cc-pVTZ+d basis set leads to comparable results to the corresponding Pople set. In fact, when we make the comparison for UCMP-DHDFT and SCS-DHDFT, we find that, although all basis sets lead to respectable MADs, the Dunning set (columns 5 and 10) somewhat outperforms the other types of basis sets. It is also noteworthy that the aug′-def2-TZVP+d basis set (columns 4 and 9) yields lower MADs than those for the def2-TZVPD′+d basis set (columns 1 and 6). Rappoport and Furche have pointed out the potential difficulty of the smaller set of diffuse functions in def2-TZVPD for describing more demanding systems, such as anions.[37] Our observation is consistent with such a proposition.

Table 3. MADs from Experimental Values (kJ mol^{-1}) for the G2/97 Set and its Subsets for B2K-PLYP-Type Procedures

	frozen core		all electron	
	A′VTZ+d	AVQZ+d	A′VTZ+d	AVQZ+d
		B2K-PLYP		
G2/97	17.6	9.5	9.7	7.7
ΔH_f	26.7	11.2	10.8	7.7
IE	9.5	8.5	9.2	8.3
EA	8.5	7.4	8.4	7.3
PA	5.2	5.2	4.8	4.9
		UCMP-B2K-PLYP[a]		
G2/97	6.6	6.6	7.8	7.7
ΔH_f	5.7	5.8	7.5	7.7
IE	7.9	7.9	8.5	8.3
EA	7.0	6.7	7.7	7.3
PA	5.5	5.3	4.8	5.0
		SCS-B2K-PLYP[b]		
G2/97	6.1	6.4	7.5	7.6
ΔH_f	5.0	5.5	7.0	7.5
IE	7.7	7.9	8.6	8.3
EA	6.7	6.6	7.7	7.3
PA	4.9	4.9	4.6	4.7
timing[c]	2.8	64.5	3.2	70.6

[a] Each c_{MP2} parameter is optimized for the specific basis set and core-correlation options. [b] The c_{OS} and c_{SS} parameters are optimized for each method. [c] Relative to the total time for B2-PLYP/(A)VTZ calculations for the G2/97 set.

While the aug′-cc-pVTZ+d basis set yields the lowest MADs for SCS-DHDFT, and we deem its use sufficiently economical for a wide range of applications, we note that the use of the 6-311+G(3df,2p)+d basis is also cost-effective. It offers further savings in computational resources over the Dunning set, but its performance is slightly worse.

Turning our attention to the effect of the amount of wave function contribution on the performance of the DHDFT procedures (Table 2), we find that B2-PLYP gives lower MADs than those for B2K-PLYP. On the other hand, it can be seen that UCMP-B2K-PLYP outperforms UCMP-B2-PLYP, and likewise SCS-B2K-PLYP yields lower MADs than those for SCS-B2-PLYP. These observations are also consistent with the results in Table 1 (columns 1 and 12). Overall, we find the combination of SCS-B2K-PLYP and aug′-cc-pVTZ+d (Table 2, column 10) gives the lowest MAD of 6.1 kJ mol^{-1} for the G2/97 set of energies. At the other end of the spectrum, it is striking that if one employs B2K-PLYP with the def2-TZVPD′+d basis set (column 6), a substantially larger MAD of 26.0 kJ mol^{-1} is obtained! This emphasizes the importance of carefully choosing the combination of method and basis set.

At this point it is instructive to summarize our observations so far. We find that the use of diffuse functions is beneficial not only for EAs but also for the calculation of ΔH_f and IE. In addition, we notice that the inclusion of excess correlation is favorable. Combining these two main ingredients and other minor details, we find that the frozen-core SCS-B2K-PLYP/aug′-cc-pVTZ+d procedure offers a cost-effective means for obtaining reliable results, with an MAD of 6.1 kJ mol^{-1} for the G2/97 test set.

Table 4. MADs from Experimental Values (kJ mol^{-1}) of Various Combinations of c_{OS} and c_{SS} Parameters, Core-Correlation Options^a and Basis Sets for SCS-B2K-PLYP on the G2/97 Set

parameter optimization level	basis set and core-correlation options			
	A′VTZ+d (FC)	AVQZ+d (FC)	A′VTZ+d (FU)	AVQZ+d (FU)
		G2/97		
A′VTZ+d (FC)	6.1	12.6	15.3	17.8
AVQZ+d (FC)	13.0	6.4	8.8	10.1
A′VTZ+d (FU)	13.8	6.5	7.5	9.6
AVQZ+d (FU)	17.8	9.5	8.3	7.6
		ΔH_f		
A′VTZ+d (FC)	5.0	18.2	24.0	28.7
AVQZ+d (FC)	18.1	5.5	9.9	13.0
A′VTZ+d (FU)	19.6	5.6	7.0	12.0
AVQZ+d (FU)	27.1	11.1	8.2	7.5
		IE, EA, and PA		
A′VTZ+d (FC)	7.2	7.2	6.9	7.3
AVQZ+d (FC)	8.1	7.3	7.7	7.2
A′VTZ+d (FU)	8.2	7.3	8.0	7.3
AVQZ+d (FU)	8.9	7.8	8.5	7.7

^{a} FC = frozen-core, and FU = full, i.e., all electrons.

On the other hand, from Table 1, we see that the use of (aug-)cc-pVQZ (column 4) offers a noteworthy improvement over (aug-)cc-pVTZ. It is reasonable to ask: are we able to further improve the performance by using aug-cc-pVQZ+d instead of aug′-cc-pVTZ+d? In order to address this question, we have carried out investigations in which we have examined both frozen-core and all-electron B2K-PLYP-type procedures. The results are shown in Table 3.

We can see that, for frozen-core B2K-PLYP, there is a substantial improvement in going from aug′-cc-pVTZ+d to aug-cc-pVQZ+d. This can mainly be attributed to poor ΔH_f predictions with frozen-core B2K-PLYP when the aug′-cc-pVTZ+d basis set is used. The corresponding improvement for all-electron B2K-PLYP is much smaller. In particular, all-electron B2K-PLYP/aug′-cc-pVTZ+d gives an MAD for ΔH_f (10.8 kJ mol^{-1}) that is somewhat larger than that for all-electron B2K-PLYP/aug-cc-pVQZ+d (7.7 kJ mol^{-1}) but much smaller than that for frozen-core B2K-PLYP/aug′-cc-pVTZ+d (26.7 kJ mol^{-1}). For UCMP-B2K-PLYP and SCS-B2K-PLYP with either frozen-core or all-electron MP2, the use of aug-cc-pVQZ+d yields results that are very similar to those obtained with aug′-cc-pVTZ+d. In comparing the performance of the frozen-core calculations with their all-electron counterparts, we find that, for B2K-PLYP, the use of all electrons in the MP2 treatment leads to lower MADs. On the other hand, the performance in fact slightly deteriorates for UCMP-B2K-PLYP and SCS-B2K-PLYP when one employs all-electron MP2. This is consistent with the observations in Table 1 (columns 1 and 2). Remarkably, the best combination of correlation treatment, theoretical method, and basis set remains frozen-core SCS-B2K-PLYP/aug′-cc-pVTZ+d.

Dependence of Performance on Optimized Parameters. When the empirical parameters in a procedure are optimized under a certain set of conditions, one potential pitfall is that the resulting method may not be able to adapt to a different set of conditions. For example, does the performance of the SCS-B2K-PLYP/aug′-cc-pVTZ+d procedure change significantly when a different basis set is used, but the c_{OS} and c_{SS} parameters optimized for aug′-cc-pVTZ+d are retained? Indeed, the desirability of using a basis set for which a DHDFT method is parametrized has been emphasized previously.[5,6,11] To this end, we have assessed the sensitivity of the performance of SCS-B2K-PLYP to different combinations of core-correlation options (frozen-core or all-electron) and basis sets (aug′-cc-pVTZ+d or aug-cc-pVQZ+d), with parameters optimized for the various core-correlation options and basis sets (Table 4).

We find that there is a large variation in the MADs for the G2/97 set for the different combinations, in which the performance of the procedure can deteriorate significantly when a set of mismatched parameters is used with certain combinations of core-correlation and basis-set options. The situation is worst when one stretches such "incompatibility" the most. Thus, the overall G2/97 MAD is largest (17.8 kJ mol^{-1}) when one employs parameters optimized for frozen-core aug′-cc-pVTZ+d but uses them in combination with all-electron aug-cc-pVQZ+d, and (coincidentally) vice versa. However, such large variations are mainly due to the differences in the performance for ΔH_f, where the use of matched parameters for frozen-core aug′-cc-pVTZ+d gives an MAD of 5.0 kJ mol^{-1}, but the use of this set of parameters for all-electron aug-cc-pVQZ+d yields the largest MAD of 28.7 kJ mol^{-1}.

On the other hand, the variation in performance for other thermochemical properties in G2/97 (IE, EA, and PA) is small, with MAD values that span a range of just 2 kJ mol^{-1}. We note that the smallest MAD for the IE, EA, and PA set of energies corresponds to the use of parameters optimized for frozen-core aug′-cc-pVTZ+d, applied to energies obtained from all-electron aug′-cc-pVTZ+d calculations. Upon inspection of the c_{OS} and c_{SS} parameters for the four procedures (Supporting Information, Table S1), we find that there is a larger variation in c_{OS} than in c_{SS}. In addition, c_{OS} is larger in magnitude than c_{SS}, and E_C^{MP2OS} is, in general, about three times larger than E_C^{MP2SS}. Thus, it appears that the variation in the $c_{OS}E_C^{MP2OS}$ term is a major contributing factor to the overall differences in the procedures.

New DuT-D3 Procedure and its Performance. Based on what we have learned from the previous sections, we have reoptimized the parameters c_{B88}, c_{HF}, c_{LYP}, c_{OS}, and c_{SS} for a B-LYP-based frozen-core SCS-DHDFT with the aug′-cc-pVTZ+d basis set. The new procedure will be referred to as DS-B-LYP/aug′-cc-pVTZ+d, owing to its similarity to DSD-B-LYP but without the D correction for dispersion.

$$E_{DS\text{-}B\text{-}LYP} = c_{B88}E_X^{B88} + c_{HF}E_X^{HF} + c_{LYP}E_C^{LYP}$$
$$+ c_{OS}E_C^{MP2OS} + c_{SS}E_C^{MP2SS} \qquad (3)$$

Within the DS label, the D relates to the double-hybrid DFT procedure, while the S relates to the use of SCS-MP2 correlation. We then supplement this method with a D3 dispersion correction and term this procedure DS-B-LYP/aug′-cc-pVTZ+d-D3. We have also optimized the parameters for the 6-311+G(3df,2p)+d basis set,[40] and the resulting methods are denoted DS-B-LYP/6-311+G(3df,2p)+d and DS-B-LYP/6-311+G(3df,2p)+d-D3. For the sake of simplicity, we will refer to DS-B-LYP/aug′-cc-pVTZ+d,

Table 5. Scale Coefficients and Parameters for the D3 Corrections for the B2K-PLYP, SCS-B2K-PLYP, DuT-D3, PoT-D3, and DSD-B-LYP-D3 Procedures

DHDFT	B2K-PLYP[a]	SCS-B2K-PLYP[b,c]	DuT-D3[b,c]	PoT-D3[c,d]	DSD-B-LYP-D3[e]
c_{B88}	0.28	0.28	0.30	0.32	0.30
c_{HF}	0.72	0.72	0.70	0.68	0.70
c_{LYP}	0.58	0.58	0.59	0.63	0.56
c_{OS}	0.42	0.48	0.47	0.46	0.46
c_{SS}	0.42	0.39	0.36	0.27	0.40
s_6	–	–	0.5	0.5	0.5
$s_{r,6}$	–	–	1.569	1.569	1.569
s_8	–	–	0.35	0.30	0.705

[a] Ref 3. [b] Optimized in conjunction with the aug′-cc-pVTZ+d basis set. [c] Frozen-core approximation for MP2 correlation. [d] Optimized for 6-311+G(3df,2p)+d. [e] Scale coefficient values for frozen-core DSD-B-LYP from ref 11 and D3 parameters from ref 12.

DS-B-LYP/aug′-cc-pVTZ+d-D3, DS-B-LYP/6-311+G(3df,2p)+d, and DS-B-LYP/6-311+G(3df,2p)+d-D3 as the DuT, DuT-D3, PoT, and PoT-D3 procedures. The DuT denotes that the first two procedures are matched to the Dunning triple-ζ basis set, and PoT signifies the use of the Pople triple-ζ basis set in the latter two.

For DHDFT procedures, the D3 correction has three adjustable parameters, namely s_6, $s_{r,6}$, and s_8.[12,23] For the DuT-D3 and PoT-D3 procedures, we initially chose the parameters determined for the DSD-B-LYP-D3 procedure,[12] with values of 0.5, 1.569, and 0.705 for s_6, $s_{r,6}$, and s_8, respectively. Examination of the effect of modifying the three D3 parameters for the DuT-D3 and PoT-D3 procedures shows that the performance of the method is relatively insensitive to the values of s_6 and $s_{r,6}$. We have therefore adopted the DSD-B-LYP-D3 s_6 and $s_{r,6}$ values for both DuT-D3 and PoT-D3. On the other hand, altering the s_8 parameter has a greater influence on the results obtained with DuT-D3 and PoT-D3. In particular, we find that a smaller value of s_8 gives a more uniformly satisfactory description for the range of thermochemical properties considered in the present study. Thus, we have chosen values for s_8 of 0.35 and 0.30 for the DuT-D3 and PoT-D3 procedures, respectively.

We have also examined the effect of using the new D3(BJ) form[41] of dispersion correction. It makes use of the damping function of Becke and Johnson,[42] instead of the form of Chai and Head-Gordon[43] that is employed in the original D3 formulation. We find that, in general, D3 and D3(BJ) give comparable results when used in conjunction with DuT and PoT. The use of D3(BJ) gives a more noticeable improvement for the MB08 set, but this comes at the expense of a small but evidently worse performance on the S22 and Grubbs sets. Taking these results into account, we have opted for the original Chai and Head-Gordon approach for the DuT-D3 and PoT-D3 procedures.

While our discussion will mainly focus on DuT-D3 due to its higher accuracy, we note that, for the largest E3 test set that we used in the present study (see below), the DuT-D3 procedure is 3.4 times more expensive than the PoT-D3 procedure, while the latter has an MAD that is only 0.7 kJ mol^{-1} larger than that for the former. We thus repeat our recommendation for the use of 6-311+G(3df,2p)+d, i.e., the PoT-D3 procedure, when the use of aug′-cc-pVTZ+d in DuT-D3 becomes computationally too demanding. The optimized parameters for DuT-D3 and PoT-D3 are

Table 6. Performance of the DuT-D3 Procedure for the E3 Test Set[a,b]

statistics	MAD	MD	LD	SD	NO
E3	7.9	−4.4	−60.9	11.3	183
E2[c]	5.9	−1.7	−49.0	8.7	88
E0	6.5	−2.8	−49.0	10.0	26
W4/08	8.5[d]	−4.3	−49.0	11.7	25
DBH24	3.7	−0.3	10.6	4.4	1
HB16	2.0	1.9	4.7	1.4	0
WI9/04	0.8	−0.6	−2.0	0.8	0
G2/97′[c]	6.2	−1.2	−42.1	8.7	45
ΔH_f	4.6	−1.0	−21.3	6.4	12
IE	7.7	−2.5	−42.1	10.6	23
EA	6.5	1.0	39.8	9.1	9
PA	4.9	−4.1	−10.8	4.6	1
E1	4.7	−1.6	−28.7	7.0	17
G3/99′[c]	6.5	−2.4	−28.7	8.8	17
ADD	2.0	1.3	7.2	2.5	0
ABS	1.6	−0.1	−4.7	2.0	0
PR8	6.5	−6.5	−9.8	2.5	0
DSD′[e]	12.7	−10.8	−60.9	14.0	95
S22	2.1	2.1	9.2	2.9	0
MB08	15.9	−14.4	−60.9	14.1	95
Pd[f]	2.2	−1.1	−7.4	2.6	0
Grubbs[f]	3.8	3.3	8.6	3.9	0

[a] MAD = mean absolute deviation, MD = mean deviation, LD = largest deviation, and SD = standard deviation (kJ mol^{-1}); and NO = number of outliers (deviations >10 kJ mol^{-1}). [b] Geometries were obtained at the BMK/6-31+G(2df,p) level, unless otherwise noted. [c] See ref 35 for the definition of the E2 set and its subsets E0, G2/97′, and E1. [d] MAD for nonmultireference systems is 6.2 kJ mol^{-1}. [e] Literature geometries were used, see refs 19−22. [f] The aug-cc-pVTZ-PP basis set and the corresponding ECP were employed for the elements Pd and Ru.

shown in Table 5, together with those for B2K-PLYP, frozen-core SCS-B2K-PLYP/aug′-cc-pVTZ+d, and frozen-core DSD-B-LYP-D3 for comparison.

It is noteworthy that the parameters c_{B88} and c_{HF} are very similar for all these methods, despite the fact that they are determined in combination with different basis sets and fitted to different training sets. Thus, it appears that the optimal c_{B88} and c_{HF} parameters vary within a relatively narrow range for a wide variety of thermochemical properties, with values of 0.30 ± 0.02 and 0.70 ± 0.02, respectively. We can see that there is a similar proportional variation for the c_{LYP} parameter, with optimum values in the range 0.60 ± 0.04. A comparison of SCS-B2K-PLYP, DuT-D3, PoT-D3, and DSD-B-LYP-D3 shows that the optimal value for c_{OS} lies in a relatively narrow range of 0.46−0.48, but there is a larger variation for the coefficient for the same-spin component of the MP2 correlation energy. Thus, c_{SS} has values that lie between 0.27 (PoT-D3) and 0.40 (DSD-B-LYP-D3).

We now assess the performance of DuT-D3 for a wider range of systems. We employ the E2 set[35] of 526 energies as the main benchmark set. The E2 set includes the W4/08 and the DBH24 sets that are also part of the DSD set. We have also included the remaining subsets of DSD, namely the S22,[44] MB08, Pd, and Grubbs sets, in our benchmark. While the Pd and Grubbs sets represent two important applications in
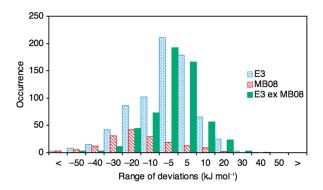
Figure 1. Distribution of the deviations (kJ mol^{-1}) for DuT-D3 for the E3, MB08, and E3 sets, excluding MB08.

transition-metal chemistry, we caution that generalization requires further investigations, especially for 3d transition metals that are not covered in the present study. The S22, MB08, Pd, and Grubbs sets comprise 214 energies, and we will refer to this collection as the DSD′ set. Thus, we have assessed the new procedure for a total of 740 energies, and we refer to this compilation of energies as the E3 set. For Pd and Ru, we have employed the aug-cc-pVTZ-PP basis set with the corresponding effective core potentials (ECPs),[45] in conjunction with aug′-cc-pVTZ+d for all the other elements. The results are shown in Table 6.

We can see that, with the exception of MB08, the MADs for all the subsets of E3 are less than 10 kJ mol^{-1}. Likewise, DuT-D3 affords SDs below 10 kJ mol^{-1} for most sets except W4/08, G2/97′ IE, and MB08. We find that the MD values for the PR8 and MB08 sets have magnitudes that are larger than 5 kJ mol^{-1}. In particular, the MB08 set is associated with an MD of −14.4 kJ mol^{-1}. This indicates systematic deviations for these sets. There are a total of 183 outliers in which the deviations are larger than 10 kJ mol^{-1}. These are dominated by outliers from the MB08 set, which account for 95 out of the total.

Figure 1 shows the distribution of the deviations for the E3, MB08, and E3 sets, excluding MB08. We can see that there are indeed systematic deviations for the MB08 set. On the other hand, the deviations for the rest of the subsets in E3 are normally distributed around zero. Thus, we find that the MD for the E3 set when MB08 is excluded is −1.5 kJ mol^{-1}, compared with −4.4 kJ mol^{-1} when MB08 is included in the analysis. Other subsets that represent substantial challenges to the DuT-D3 procedure, in terms of the number of outliers and largest deviations, include W4/08 (atomization energies), G2/97′ ΔH_{f_1} G3/99′ ΔH_{f_1} G2/97′ IE, and G2/97′ EA.

Comparison of DuT-D3, PoT-D3, DuT, and PoT with DSD-B-LYP and its Variants. In a recent study,[12] Goerigk and Grimme have formulated the DSD-B-LYP-D3 method and found it to be one of the best performing DHDFT procedures for the extensive GMTKN30 test set. In the present study, we employ DSD-B-LYP and DSD-B-LYP-D3 as yardsticks to further scrutinize the performance of the DuT-D3 and PoT-D3 procedures and their pure quantum mechanical variants, i.e., DuT and PoT. We have also examined the effect of removing the dispersion term in DSD-B-LYP altogether, and we refer to this method as DSD-B-LYP(ex D).

We have employed two quadruple-ζ basis sets, namely aug′-pc3+d and aug′-def2-QZVP, for the calculation of the quantum mechanical component of DSD-B-LYP and DSD-B-LYP-D3.

The aug′-pc3+d basis set was chosen because it is one of the major basis sets employed in the original parametrization of DSD-B-LYP.[11] The remaining basis sets utilized in the formulation of DSD-B-LYP are Ahlrichs-style basis sets def2-TZVP, def2-QZVP, and def2-QZVPP. Among these, the def2-QZVP basis set was also used for the evaluation of DSD-B-LYP-D3, and this combination shows promising results.[12] In the present study, we augment the def2-QZVP basis set with diffuse functions from aug′-cc-pVQZ to arrive at the aug′-def2-QZVP basis set, and we examine its performance when used in conjunction with DSD-B-LYP and DSD-B-LYP-D3. The frozen-core approximation was applied, as the inclusion of all electrons for SCS-MP2 correlation in the context of the DHDFT procedure has been shown to lead to only a small improvement in performance (ref 11 and Table 3). The MADs for the E3 set and its subsets are summarized in Table 7.

We first note that, in general, all combinations of methods and basis sets perform comparably. Among the two basis sets employed for the DSD-B-LYP-type procedures, the use of the aug′-def2-QZVP basis set (columns 6, 8, and 10) typically yields results that are slightly better than those for aug′-pc3+d (columns 5, 7, and 9). In addition, the use of the aug′-def2-QZVP basis set offers a notable saving in computational resources compared with aug′-pc3+d, with timing ratios of 26.4× and 45.9× relative to PoT, for aug′-def2-QZVP and aug′-pc3+d, respectively, for the E2 set. While a generalization of the above observations would require further investigations, nonetheless the aug′-def2-QZVP basis set appears to be a more suitable and cost-effective quadruple-ζ basis set for DSD-B-LYP-type procedures than aug′-pc3+d.

A comparison of DuT-D3 with PoT-D3 and DuT with PoT shows that, for each subset, the DuT procedures (columns 1 and 3) generally outperform the PoT variants (columns 2 and 4), with MAD values that are lower than those for the corresponding PoT procedures by up to 2 kJ mol^{-1}. Cases where PoT-D3 and PoT gives MADs that are larger than those for the respective DuT procedures by more than 2 kJ mol^{-1} include W4/08, G3/99′, and the Grubbs set. Among these three sets, the largest MADs occur for the W4/08 set, in which DuT-D3 yields an MAD of 8.5 kJ mol^{-1}, while the corresponding value for PoT-D3 is 10.8 kJ mol^{-1}. On the other hand, PoT-D3 performs better than DuT-D3 for the PR8 and MB08 sets. In general, we find that the inclusion of D3 corrections (columns 1 and 2) leads to comparable or lower MADs than those for DuT and PoT (columns 3 and 4). Only very minor deterioration in the performance is observed for the DBH24, G2/97′ ΔH_{f_1} and PR8 sets when dispersion corrections are included. Nonetheless, we emphasize the general good performance of all four DS-B-LYP-type procedures, namely DuT-D3, PoT-D3, DuT, and PoT, such that a large part of the chemistry can be captured with quantum mechanics without the requirement for additional dispersion corrections.

We now compare the performance of DuT-D3 and DuT with the performances of the three variants of DSD-B-LYP (Table 7). We find that the procedures that do not include a dispersion correction, i.e., DuT (column 3) and DSD-B-LYP(ex D) (columns 9 and 10) generally give MAD values that are similar to one another for each subset, with the G2/97′ ΔH_{f_1} G3/99′, S22, and Grubbs sets being notable exceptions. Likewise, the two dispersion-corrected variants of DSD-B-LYP (columns 5 and 6 for DSD-B-LYP and columns 7 and 8 for DSD-B-LYP-D3) have performances that are comparable, except for the G3/99′ and Grubbs sets. However, there are more substantial differences

Table 7. Comparison of MADs from Benchmark Values (kJ mol^{-1}) for the E3 Test Set for DuT-D3, PoT-D3, DuT, PoT, DSD-B-LYP, DSD-B-LYP-D3, and DSD-B-LYP(ex D)[a]

	1	2	3	4	5	6	7	8	9	10
DHDFT	DuT-D3	PoT-D3	DuT	PoT	DSD-B-LYP		DSD-B-LYP-D3		DSD-B-LYP(ex D)	
basis set	A'VTZ +d[b]	6-311+G (3df,2p)+d[c]	A'VTZ +d[b]	6-311+G (3df,2p)+d[c]	aug'-pc3 +d	aug'-def2-QZVP	aug'-pc3 +d	aug'-def2-QZVP	aug'-pc3 +d	aug'-def2-QZVP
D Correction	D3	D3	nil	nil	D		D3		nil	
E3	7.9	8.6	8.4	9.0	9.3	9.0	9.0	8.7	9.2	9.1
E2	5.9	7.3	6.0	7.4	8.4	7.9	7.8	7.4	6.9	6.7
E0	6.5	8.2	6.5	8.2	6.7	6.5	6.6	6.4	6.5	6.3
W4/08	8.5	10.8	8.5	10.8	8.9	8.4	8.8	8.3	8.7	8.3
DBH24	3.7	3.7	3.5	3.7	3.2	3.7	3.2	3.7	3.1	3.4
HB16	2.0	2.6	1.6	2.2	1.8	2.0	1.6	1.8	0.9	1.1
WI9/04	0.8	0.8	1.0	1.0	0.8	0.8	0.8	0.8	1.0	1.0
G2/97'	6.2	7.4	6.1	7.4	8.0	7.6	7.7	7.3	7.0	6.8
ΔH_f	4.6	6.5	4.4	6.4	9.2	8.5	8.4	7.7	6.7	6.3
IE	7.7	8.4	7.7	8.4	8.0	7.7	8.0	7.7	8.0	7.7
EA	6.5	7.7	6.5	7.7	6.4	6.3	6.4	6.3	6.4	6.3
PA	4.9	5.0	4.9	5.0	4.4	4.8	4.6	5.1	4.6	5.1
E1	4.7	5.9	5.1	6.4	11.0	10.2	9.4	8.7	7.0	6.9
G3/99'	6.5	8.8	7.0	9.3	17.4	16.0	14.8	13.4	10.1	9.8
ADD	2.0	3.1	3.1	4.3	2.0	2.1	1.8	1.8	3.9	3.8
ABS	1.6	1.5	1.7	1.7	1.6	1.7	1.6	1.6	1.9	1.8
PR8	6.5	1.9	5.4	1.7	9.2	9.6	7.6	8.0	5.5	5.9
DSD'	12.7	11.9	14.4	13.2	11.8		11.8		15.0	
S22	2.1	2.5	4.9	4.8	1.3[d,g,h]		1.7[d,i,h]		6.5[d,j,h]	
MB08	15.9	14.4	17.5	15.6	14.6[e,g]		14.5[e,i]		17.7[e,j]	
Pd	2.2	3.9	2.5	4.1	2.8[f,g]		2.9[f,i]		3.2[f,j]	
Grubbs	3.8	7.5	7.2	11.0	3.6[d,g]		6.1[d,i]		13.4[d,j]	
timing (E2)[k]	2.8	1.0	2.8	1.0	46.4	26.4	46.4	26.4	46.4	26.4
timing (E3)[k]	3.4	1.0	3.4	1.0	—	—	—	—	—	—

[a] The frozen-core approximation is employed for all methods. [b] The aug-cc-pVTZ-PP basis set was used for Pd and Ru. [c] The aug-def2-TZVP basis set was used for Pd and Ru. [d] Values for the def2-TZVP basis set. [e] Values for the def2-QZVP basis set. [f] Values for the def2-QZVPP basis set. [g] Obtained from literature deviations reported in the Supporting Information of ref 11. [h] Revised for updated benchmark values from ref 19b. [i] Deviations obtained by adding the D3 − D contributions to the literature values (ref 11). [j] Deviations obtained by subtracting the D contributions from the literature values (ref 11). [k] Relative to the total time for PoT calculations for the designated test set.

between DSD-B-LYP(ex D) (columns 9 and 10) and DSD-B-LYP (columns 5 and 6), notably for the G3/99', S22, and Grubbs sets. These results highlight the significant contribution of empirical dispersion corrections to the relative energies in the DSD-B-LYP method. Overall, we find that there are large variations for the G3/99', PR8, S22, and Grubbs sets between the various methods.

What factors contribute to the more significant variations in these sets? The G3/99' set contains ΔH_f values for medium-sized molecules. One can expect large variations in the performance of different methods for ΔH_f and that the differences grow with the size of the molecules. In addition, the dispersion correction for ΔH_f would also grow with the size of the molecule, as the product atoms contain a zero dispersion term. For instance, there is a D correction (for DSD-B-LYP) of −26.1 kJ mol^{-1} and a D3 correction (for DSD-B-LYP-D3) of −17.3 kJ mol^{-1} for the ΔH_f of n-octane.[46] Therefore, we see large variations for G3/99', and the inclusion of the particular dispersion corrections appears to lead to larger MADs for DSD-B-LYP and DSD-B-LYP-D3.

The S22 set includes complexation energies between large monomers, while the PR8 and Grubbs sets comprise barriers and reaction energies with large reactants. In these cases, we also see the sizable contributions of large empirical dispersion corrections to the DSD-B-LYP energies, which lead to larger MADs for PR8 but smaller MADs for the S22 and the Grubbs sets. To illustrate the large dispersion corrections for some of the species in the S22 set, for example, for DSD-B-LYP and DSD-B-LYP-D3, the adenine-thymine stacked dimer has a D correction of −18.0 kJ mol^{-1} and a D3 correction of −15.2 kJ mol^{-1} to the binding energy.[47] In this case, the dispersion corrections lead to improved results. In addition, for the Grubbs set, 6 out of the 7 entries in the set have D contributions to relative energies that exceed 10 kJ mol^{-1}, and these D corrections contribute significantly to the difference in the MADs of the DSD-B-LYP(ex D) and DSD-B-LYP methods.

We now rank the performance of these methods. Overall, DuT-D3 yields the smallest MAD for the complete E3 set, although the other procedures follow closely. When compared with the DSD-B-LYP variants, the better performance of

2860

dx.doi.org/10.1021/ct200396x |J. Chem. Theory Comput. 2011, 7, 2852–2863

Table 8. Comparison of MADs from Benchmark Values (kJ mol^{-1}) for Selected Subsets of the E3 Test Set for ωB97X-2(LP), DuT-D3, PoT-D3, DSD-B-LYP(ex D), DSD-B-LYP, and DSD-B-LYP-D3

	1[a]	2	3	4	5	6	7	8	9
DHDFT	ωB97X-2(LP)	DuT-D3	PoT-D3	DSD-B-LYP(ex D)		DSD-B-LYP		DSD-B-LYP-D3	
basis set	6-311++G (3df,3pd)	A'VTZ +d	6-311+G (3df,2p)+d	aug'-pc3 +d	aug'-def2-QZVP	aug'-pc3 +d	aug'-def2-QZVP	aug'-pc3 +d	aug'-def2-QZVP
D Correction	nil	D3	D3	nil		D		D3	
G2/97 and G3/99 ΔH_f	6.4	5.6	7.7	8.1	7.7	11.6	10.7	10.4	9.6
G2-1 IE	7.2	7.0	7.8	7.3	6.8	7.3	6.8	7.3	6.8
G2-1 EA	6.5	5.8	9.2	6.0	5.4	6.0	5.4	6.0	5.4
G2/97 PA	4.6	4.9	5.0	4.6	5.1	4.4	4.8	4.6	5.1
S22	1.0[b]	2.3	2.7	6.7	6.7	1.2	1.2	1.7	1.7

[a] MAD values obtained from ref 6. [b] Value corresponds to deviations from benchmark values from ref 19a.

DuT-D3 can primarily be attributed to the much smaller deviations for the G3/99' set, while maintaining its robustness for the other sets. It is thus important to note that, for DHDFT procedures, the use of appropriate triple-ζ basis sets, such as aug'-cc-pVTZ+d and 6-311+G(3df,2p)+d in this instance, can yield results that are of comparable reliability to those obtained with quadruple-ζ basis sets but at considerably lower computational expense.

We have also compared (Table 8) the performance of the very promising ωB97X-2(LP)/6-311++G(3df,3pd) procedure with the performances for the methods, listed in Table 7, on a selected subset of E3, namely G2/97 and G3/99 ΔH_f, the G2-1 subsets[15] of G2/97 IE and G2/97 EA, G2/97 PA, and S22. It can be seen that all three procedures that employ triple-ζ basis sets (columns 1−3) are competitive in performance with the DSD-B-LYP variants (columns 4−9) that use quadruple-ζ basis sets. This provides further support for the use of appropriate triple-ζ basis sets for DHDFT calculations.

It can be seen (Table 8) that the procedures that do not include an explicit dispersion correction or those that include dispersion corrections with smaller s_8 contributions (columns 1−5) are characterized by smaller MADs for the G2/97 and G3/99 ΔH_fs and, in general, by larger MADs for the S22 set. On the other hand, the procedures that include a larger dispersion correction (columns 6−9) are characterized by larger MADs for the G2/97 and G3/99 ΔH_fs and smaller MADs for the S22 set. It is notable that ωB97X-2(LP)/6-311++G(3df,3pd) performs well for both the ΔH_f sets and the S22 set, presumably because of the incorporation of long-range corrections through its range-separation scheme.[6]

CONCLUDING REMARKS

In the present investigation, we have examined a variety of B-LYP-based DHDFT procedures used in conjunction with a range of basis sets, particularly triple-ζ basis sets. The following important points emerge from our study:

(1) We find that the optimal %E_X^{B88} and %E_X^{HF} are ~30 and 70%, respectively, and these values are relatively insensitive to the thermochemical properties of interest. We also find that it is beneficial to include correlation energy in excess of the amount constrained by the requirement of %E_C^{LYP} + %E_C^{MP2} = 100%. For the energies in the G2/97 set, the use of SCS-MP2 yields comparable or slightly

better results than the use of conventional MP2. We find the optimal %E_C^{MP2OS} to be ~47%, while %E_C^{MP2SS} lies between 27 and 40%.

(2) Regarding the basis set, the use of diffuse functions on nonhydrogen atoms appears to be important not only for the evaluation of EAs but also for other thermochemical properties, such as ΔH_f and IE. However, the inclusion of diffuse functions on hydrogen is not essential. On the other hand, we deem the use of tight d functions on second-row atoms a cost-effective improvement. Among the different styles of augmented triple-ζ-type basis sets examined, namely the Pople 6-311+G(3df,2p)+d, Dunning aug'-cc-pVTZ+d, Jensen aug'-pc2+d, and Ahlrichs def2-TZVPD'+d and aug'-def2-TZVP+d sets, the aug'-cc-pVTZ+d basis set emerges as the best-performing basis set for B-LYP-based DHDFT methods. The use of the 6-311+G(3df,2p)+d basis set gives slightly less accurate results but offers notable savings in computer time. When used in conjunction with UCMP-B2K-PLYP and SCS-B2K-PLYP procedures, aug'-cc-pVTZ+d somewhat outperforms the larger aug-cc-pVQZ+d basis set for the G2/97 set.

(3) We find that when a set of SCS parameters is optimized for a specific basis set, its use with a different basis set can lead to large deviations for heats of formation, while other relative energies are less sensitive to the combination of parameters and basis set. We recommend the use in general of matching optimum parameters and basis sets.

(4) Using aug'-cc-pVTZ+d, we have formulated the DuT-D3 and DuT DHDFT procedures. For the larger E2 and E3 test sets, DuT-D3 and DuT perform comparably to DSD-B-LYP-D3 and DSD-B-LYP when the latter are used in conjunction with the quadruple-ζ basis sets for which they are developed, namely aug'-pc3+d and aug'-def2-QZVP. However, the computational expense of DuT-D3 and DuT is significantly lower. This supports the use of appropriate and cost-effective triple-ζ basis sets for DHDFT calculations.

(5) We have also formulated the PoT-D3 and PoT DHDFT procedures with the 6-311+G(3df,2p)+d basis set. These are only slightly less accurate than the DuT variants, but the smaller basis set enables calculations on larger systems.

2861

dx.doi.org/10.1021/ct200396x |J. Chem. Theory Comput. 2011, 7, 2852–2863

The previously formulated ωB97X-2(LP)/6-311++G-(3df,3pd) method also performs particularly well.

■ ASSOCIATED CONTENT

S **Supporting Information.** Optimized MP2 parameters for the various DHDFT procedures (Table S1), total DuT and PoT electronic energies and associated D3 corrections (Tables S2−S17), and deviations from benchmark values for DuT-D3 and PoT-D3 (Tables S18−S32). Also included are the aug′-cc-pVTZ+d (for the DuT procedure) and 6-311+G(3df,2p)+d) (for the PoT procedure) basis sets in Gaussian 09 format, along with input examples for performing DuT and PoT calculations with Gaussian 09. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: chan_b@chem.usyd.edu.au; radom@chem.usyd.edu.au.

■ ACKNOWLEDGMENT

■ REFERENCES

(1) Grimme, S. *J. Chem. Phys.* **2006**, *124*, 034108.

(2) Grimme, S.; Schwabe, T. *Phys. Chem. Chem. Phys.* **2006**, *8*, 4398.

(3) Tarnopolsky, A.; Karton, A.; Sertchook, R.; Vuzman, D.; Martin, J. M. L. *J. Phys. Chem. A* **2008**, *112*, 3.

(4) Karton, A.; Tarnopolsky, A.; Lamere, J. F.; Schatz, G. C.; Martin, J. M. L. *J. Phys. Chem. A* **2008**, *112*, 12868.

(5) Benighaus, T.; Lochan, R. C.; Chai, J.-D.; Head-Gordon, M. *J. Phys. Chem. A* **2008**, *112*, 2702.

(6) Chai, J.-D.; Head-Gordon, M. *J. Chem. Phys.* **2009**, *131*, 174105.

(7) Graham, D. C.; Menon, A. S.; Goerigk, L.; Grimme, S.; Radom, L. *J. Phys. Chem. A* **2009**, *113*, 9861.

(8) Zhang, Y.; Xu, X.; Goddard, W. A., III *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 4963.

(9) Zhang, I. Y.; Luo, Y.; Xu, X. *J. Chem. Phys.* **2010**, *132*, 194105.

(10) Zhang, I. Y.; Luo, Y.; Xu, X. *J. Chem. Phys.* **2010**, *133*, 104105.

(11) Kozuch, S.; Gruzman, D.; Martin, J. M. L. *J. Phys. Chem. C* **2010**, *114*, 20801The DSD label relates to double-hybrid, SCS-MP2 correlation, and a dispersion correction.

(12) Goerigk, L.; Grimme, S. *J. Chem. Theory Comput.* **2011**, *7*, 291.

(13) Sharkas, K.; Toulouse, J.; Savin, A. *J. Chem. Phys.* **2011**, *134*, 064113.

(14) Grimme, S.; Schwabe, T. *Acc. Chem. Res.* **2008**, *41*, 569.

(15) (a) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1997**, *106*, 1063. (b) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 42.

(16) Grimme, S. *J. Chem. Phys.* **2003**, *118*, 9095.

(17) Grimme, S. *J. Comput. Chem.* **2004**, *25*, 1463.

(18) (a) Zheng, J.; Zhao, Y.; Truhlar, D. G. *J. Chem. Theory Comput.* **2007**, *3*, 569. (b) Zheng, J.; Zhao, Y.; Truhlar, D. G. *J. Chem. Theory Comput.* **2009**, *5*, 808.

(19) (a) Jurecka, P.; Sponer, J.; Cerny, J.; Hobza, P. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1985. (b) Takatani, T.; Hohenstein, E. G.; Malagoli, M.; Marshall, M. S.; Sherrill, C. D. *J. Chem. Phys.* **2010**, *132*, 144104.

(20) Schwabe, T.; Grimme, S. *J. Phys. Chem. A* **2009**, *113*, 3005.

(21) Quintal, M. M.; Karton, A.; Iron, M. A.; Boese, A. D.; Martin, J. M. L. *J. Phys. Chem. A* **2006**, *110*, 709.

(22) Zhao, Y.; Truhlar, D. G. *J. Chem. Theory Comput.* **2009**, *5*, 324.

(23) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104.See also: http://toc.uni-muenster.de/DFTD3/index.html (accessed January 27, 2011).

(24) Weigend, F.; Furche, F.; Ahlrichs, R. *J. Chem. Phys.* **2003**, *119*, 12753.

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

(26) Dunning, T. H., Jr. *J. Chem. Phys.* **1999**, *90*, 1007.

(27) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.

(28) Hehre, W. J.; Radom, L.; Schleyer, P. v. P.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986, pp 65−88.

(29) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **2000**, *112*, 7374.

(30) For other DHDFT procedures examined in ref 12, a larger basis set effect ($\sim$0.4−0.5 kcal mol^{-1}, i.e., $\sim$1.6−2.1 kJ mol^{-1}) is found, with the quadruple-ζ basis set again performing better.

(31) See for example: (a) Hehre, W. J.; Radom, L.; Schleyer, P. v. P.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986. (b) Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*, 2nd ed.; Wiley: New York, 2001. (c) Jensen, F. *Introduction to Computational Chemistry*, 2nd ed.; Wiley: Chichester, U.K., 2007.

(32) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision E.01; Gaussian, Inc.: Wallingford, CT, 2004.

(33) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, revision A.02; Gaussian, Inc.: Wallingford, CT, 2009.

(34) Boese, A. D.; Martin, J. M. L. *J. Chem. Phys.* **2004**, *121*, 3405.

(35) Chan, B.; Deng, J.; Radom, L. *J. Chem. Theory Comput.* **2011**, *7*, 112.

(36) Merrick, J. P.; Moran, D.; Radom, L. *J. Phys. Chem. A* **2007**, *111*, 11683.

(37) Rappoport, D.; Furche, F. *J. Chem. Phys.* **2010**, *133*, 134105.

(38) (a) Feller, D. *J. Comput. Chem.* **1996**, *17*, 1571. (b) Schuchardt, K. L.; Didier, B. T.; Elsethagen, T.; Sun, L.; Gurumoorthi, V.; Chase, J.; Li, J.; Windus, T. L. *J. Chem. Inf. Model* **2007**, *47*, 1045.

(39) Martin, J. M. L. *J. Mol. Struct. (Theochem)* **2006**, *771*, 19.

(40) For the calculations that include Pd and Ru, we have employed the def2-TZVP basis set for these two elements, augmented with diffuse functions from the aug-cc-pVTZ-PP basis set. The def2-TZVP ECPs are used for Pd and Ru. This basis set is chosen as its performance and computational cost are close to those for 6-311+G(3df,2p)+d (Table 2).

(41) Grimme, S.; Ehrlich, S.; Goerigk, L. *J. Comput. Chem.* **2011**, *32*, 1456.

(42) (a) Becke, A. D.; Johnson, E. R. *J. Chem. Phys.* **2005**, *122*, 154101. (b) Johnson, E. R.; Becke, A. D. *J. Chem. Phys.* **2005**, *123*, 024101. (c) Johnson, E. R.; Becke, A. D. *J. Chem. Phys.* **2006**, *124*, 174104.

(43) Chai, J.-D.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615.

(44) Unless otherwise noted, for the S22 set, we have employed the revised values from ref 19b.

(45) Peterson, K. A.; Figgen, D.; Dolg, M.; Stoll, H. *J. Chem. Phys.* **2007**, *126*, 124101.

(46) The calculated ΔH_f values for *n*-octane are -214.0 (DuT-D3), -207.8 (PoT-D3), -204.8 (DuT), -199.7 (PoT), -227.3 (DSD-B-LYP/aug$'$-def2-QZVP), -218.5 (DSD-B-LYP-D3/aug$'$-def2-QZVP), and -201.2 (DSD-B-LYP(ex D)/aug$'$-def2-QZVP) kJ mol^{-1}, compared with the experimental value of -208.8 kJ mol^{-1}.

(47) The reference value for the adenine-thymine stacked dimer binding energy is -48.8 kJ mol^{-1}. The calculated values are -45.6 (DuT-D3), -44.1 (PoT-D3), -36.9 (DuT), -36.4 (PoT), -48.5 (DSD-B-LYP/def2-TZVP), -45.6 (DSD-B-LYP-D3/def2-TZVP), and -30.4 (DSD-B-LYP(ex D)/def2-TZVP) kJ mol^{-1}. The values for DSD-B-LYP, DSD-B-LYP-D3, and DSD-B-LYP(ex D) were evaluated using data given in the Supporting Information of ref 11.

2863

dx.doi.org/10.1021/ct200396x |*J. Chem. Theory Comput.* 2011, 7, 2852–2863