

# **Highly accurate CCSDT(Q)/CBS reaction barrier heights for a diverse set of transition structures: Basis set convergence and cost-effective approaches for estimating post-CCSD(T) contributions**

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## **ABSTRACT**

The ability to accurately calculate reaction barrier heights is of central importance to many areas of chemistry. We report an extensive study examining the basis set convergence of post-CCSD(T) contributions (up to CCSDT(Q)) for a diverse set of 28 reaction barrier heights. In contrast to previous studies, we focus here on larger transition structures (TSs) involving 4–7 non-hydrogen atoms. The set of reaction barrier heights includes pericyclic, bipolar cycloaddition, cycloreversion, and multiple proton transfer reactions. We find that in most cases post-CCSD(T) contributions converge rapidly towards the basis set limit, such that even double- $\zeta$  and truncated double- $\zeta$  basis sets provide useful estimates of the T–(T) and (Q) contributions, respectively. In addition, we find that due to the tendency of these small basis sets to systematically underestimate the T–(T) and (Q) components, scaling is an effective approach for improving performance. For example, scaling the T–(T)/cc-pVDZ contribution by 1.25 results in an RMSD of merely 0.4 kJ mol<sup>−1</sup> relative to basis set limit reference values from W3lite-F12

theory. Similarly, calculating the (Q) contribution with a cc-pVDZ basis set without d functions and scaling by 1.6 results in an RMSD of 0.5 kJ mol<sup>-1</sup>. We also examine the magnitude of post-CCSD(T) contributions for a wide range of TSs. We find that for pericyclic, bipolar cycloaddition, and multiple proton transfer reactions there is an effective cancellation between the T–(T) and (Q) components (i.e., they have opposite signs and are of similar magnitude), such that overall post-CCSD(T) contributions to the reaction barrier heights are below ~1 kJ mol<sup>-1</sup> (in absolute value). However, for the barrier heights of cycloreversion reactions, the T–(T) and (Q) components are both negative and large and consequentially post-CCSD(T) contributions reduce the reaction barrier heights by significant amounts ranging between 4.1–6.7 kJ mol<sup>-1</sup>.

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Keywords: Coupled Cluster Theory; CCSDT(Q); CCSD(T); Barrier Heights.

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## 1. Introduction

A reaction barrier height is the most basic chemical quantity affecting the kinetics of chemical reactions. Coupled-cluster (CC) theory is one of the most cost-effective methods for obtaining highly accurate reaction barrier heights.<sup>1,2,3,4,5</sup> In particular, the CCSD(T) method (i.e., CC with single, double, and quasiperturbative triple excitations)<sup>6,7,8</sup> has been extensively used for obtaining reaction barrier heights in a wide range of chemical systems (for a few recent examples see refs. 9,10,11,12,13,14,15,16,17,18,19,20,21,22,23,24). With the increase in available computational power and efficiency of quantum chemical codes, the calculation of reaction barrier heights with higher-order CC methods (normally up to CCSDT(Q)) has become more prevalent over the past decade. Normally, the CCSDT(Q) method is used for investigating relatively small transition structures (TSs) with pronounced multireference character. For instance, for reactions involving oxygen-rich species<sup>25,26,27,28,29,30,31,32,33,34,35,36,37</sup> and other small TSs.<sup>38,39,40,41,42,43,44, 45,46,47</sup>

The aim of the present work is to provide a systematic examination of basis set convergence of post-CCSD contributions (up to CCSDT(Q)) for a diverse set of reaction barrier heights. In contrast to previous basis set convergence studies, which considered small TSs mostly with 1–3 non-hydrogen atoms,<sup>48,49,50</sup> here we focus on larger TSs involving 4–7 non-hydrogen atoms. This enables us to consider a diverse set of chemically more complex TSs, including pericyclic, bipolar cycloaddition, cycloreversion, and multiple proton transfer TSs.

We use the high-level composite W3lite-F12 theory<sup>51,52,53</sup> to calculate the barrier heights for a diverse set of 28 reaction barrier heights at the CCSDT(Q)/CBS level of theory (i.e., CC with single, double, triple, and quasiperturbative quadruple excitations at the complete basis set limit). We begin by evaluating the performance of W3lite-F12 theory against the highly accurate reaction barrier heights in the DBH24/08 database,<sup>38,48</sup> which were mostly obtained at the CCSDTQ5/CBS level via W4 theory.<sup>54,55,56</sup> We find that W3lite-F12 theory attains a root mean

square deviation (RMSD) of 0.9 kJ mol<sup>-1</sup> for the reaction barrier heights in the DBH24/08 database indicating it is suitable for obtaining benchmark reference reaction barrier heights. We proceed to calculate W3lite-F12 reference reaction barrier heights for a diverse set of 28 reaction barrier heights involving larger and more complex TSs. We use these reference benchmark reaction barrier heights to examine the basis set convergence and magnitude of post-CCSD(T) contributions to reaction barrier heights and offer cost-effective approaches for estimating post-CCSD(T) contributions using relatively small basis sets.

## 2. Computational Methods

All the CCSD(T) calculations were carried out using the Molpro 2016 program suite.<sup>57,58</sup> All post-CCSD(T) calculations were performed using the MRCC program.<sup>59,60</sup> Unless otherwise noted, all calculations are carried out in conjunction with the correlation-consistent basis sets of Dunning and co-workers.<sup>61,62,63</sup> For the sake of brevity, the combination of the cc-pVnZ basis sets on H and first-row elements with the cc-pV(n+d)Z basis set on second-row elements is denoted by VnZ. Likewise, the combination of cc-pVnZ on H, aug-cc-pVnZ on first-row elements, and aug-cc-pV(n+d)Z on second-row elements is denoted by A'VnZ (this combination is also commonly denoted by jul-cc-pVnZ).<sup>64</sup> In addition, we use three truncated versions of these basis sets. The VDZ(p) basis set is a truncated version of the VDZ basis set without the d functions. We also consider a minimal basis set which additionally omits another set of s and p functions from the VDZ(p) basis set, this basis set will simply be referred to as MIN. The VTZ(1d) basis set is a truncated version of the VTZ basis set in which the sp functions from the VTZ basis set are combined with the d functions from the VDZ basis set.

Unless otherwise indicated, all basis set extrapolations employ the  $E(L) = E_{\infty} + A/L^{\alpha}$  two-point extrapolation formula with  $\alpha = 5$  in Hartree–Fock (HF) and  $\alpha = 3$  in correlated calculations (where  $L$  is the highest angular momentum represented in the basis sets for the non-hydrogen

atoms). Basis set extrapolations using the  $VnZ$  and  $V(n+1)Z$  basis sets are denoted by  $V\{n,n+1\}Z$ . For the CCSDT–CCSD(T) contribution we also consider an extrapolation employing the VDZ(p) and VDZ basis sets, which is not dependant on the  $L$ , as prescribed in W3.2lite theory.<sup>51</sup>

We use W3lite-F12 theory for obtaining benchmark reference barrier heights for the reactions in the BH28 database. The computational protocol of W3lite-F12 theory has been specified and rationalized elsewhere.<sup>51,52,53</sup> For the sake of making the paper self-contained, we briefly summarize the various steps in W3lite-F12 theory. The CCSD(T) component is taken from W2-F12 theory<sup>52</sup> and involves the following steps:

- The Hartree–Fock energy is calculated at the HF\*/VQZ-F12 level of theory,<sup>65</sup> where HF\* indicates that the complementary auxiliary basis set (CABS) singles correction is included in the self-consistent field (SCF) energy.<sup>66,67,68</sup>
- The valence CCSD-F12 correlation energy is extrapolated from the VTZ-F12 and VQZ-F12 basis sets.
- The valence (T) contribution is calculated in conjunction with the VTZ-F12 basis set.

The post-CCSD(T) contributions are taken from W3.2lite theory.<sup>51</sup> In particular:

- The higher-order triple excitations, CCSDT–CCSD(T), contribution is extrapolated from the VDZ and VTZ(1d) basis sets.
- The CCSDT(Q)–CCSDT contribution is calculated with the VDZ basis set.

In the following sections we will examine the basis set convergence of the SCF and correlation components (CCSD, (T), T–(T), and (Q)) relative to reference CBS values of the corresponding components obtained from W4, W3.2, or W3lite-F12 theory. Unless otherwise indicated, the basis set convergence of each component is examined individually, i.e., by comparison to CBS results of the same component. For example, the basis set convergence of the SCF component is

examined relative to SCF/CBS values, the basis set convergence of the CCSD correlation component is evaluated relative to CCSD/CBS values, etc.

### 3. Results and Discussion

**3.1. The DBH24 database.** Reference reaction barrier heights for the DBH24 database were calculated by means of the high-level W4 and W3.2 composite ab initio procedures in reference 38. The W4 procedure<sup>54</sup> is a cost-effective composite thermochemical protocol for obtaining the CCSDTQ5/CBS energy and has been found to achieve a  $2\sigma$  confidence interval of  $0.71 \text{ kJ mol}^{-1}$  for a set of 35 highly accurate experimental atomization energies including pathologically multireference systems such as ozone).<sup>53</sup> It should be pointed out that the reference experimental atomization energies, obtained from the active thermochemical tables (ATcT)<sup>69, 70</sup> are all associated with error bars  $\leq 0.2 \text{ kJ mol}^{-1}$ . For the same set of experimental atomization energies, the W3.2 procedure, which calculates the CCSDT(Q)/CBS energy, attains a  $2\sigma$  confidence interval of about twice as that for W4 theory, namely  $1.6 \text{ kJ mol}^{-1}$ .<sup>53</sup>

The DBH24 set consists six barrier heights for each of the following reaction types: hydrogen transfer (HT), heavy atom transfer (HAT), nucleophilic substitution (NS), and unimolecular and recombination (UAR) reactions. Ref. 38 obtains W4 barrier heights for 16 reactions (6 HT, 4 HAT, and 6 UAR), and W3.2 barrier heights for the eight remaining reactions (2 HAT and 6 NS). It is important to note that for the 16 reaction barrier heights for which both W4 and W3.2 reference values are available, the RMSD between the two sets of values is  $0.55 \text{ kJ mol}^{-1}$ , demonstrating that W3.2 can achieve sub-kilojoule-per-mol accuracy for this database. The component breakdown of the W4 and W3.2 reference values is given in Table 1. In the following sections we will use these highly accurate reference values to (i) assess the performance of W3lite-F12 theory, and (ii) examine the basis set convergence of the CCSD(T) and post-CCSD(T) components of the reaction barrier heights in the DBH24 database.

**Table 1.** Component breakdown of the W4 and W3.2 benchmark reference reaction barrier heights for the forward and reverse reactions in the DBH24 database.<sup>a</sup>

Database	TS	SCF	$\Delta\text{CCSD}$	$\Delta(\text{T})$	$\Delta\text{T}_3-(\text{T})^e$	$\Delta\text{T}_4^f$	$\Delta\text{T}_5^g$	$E_e^{\ddagger h}$	$E_e^{\ddagger i}$
Forward	<b>1</b>	146.9	-67.0	-6.8	-0.5	-1.3	-0.1	73.2	71.2
	<b>2</b>	172.5	-91.6	-6.9	-0.3	-0.4	0.0	74.0	73.3
	<b>3<sup>b</sup></b>	106.1	-62.6	-14.2	-0.2	-1.0	N/A	29.3	28.0
	<b>4<sup>b</sup></b>	70.0	-5.7	-8.0	-0.5	-0.4	N/A	56.2	55.3
	<b>5<sup>b</sup></b>	17.5	1.4	-4.8	-0.4	-0.2	N/A	14.1	13.5
	<b>6<sup>b</sup></b>	32.5	-31.2	-11.6	-0.1	-1.0	N/A	-10.3	-11.4
	<b>7</b>	135.2	-69.2	-5.5	-0.5	-0.7	0.1	60.5	59.5
	<b>8</b>	40.5	-29.8	-2.5	-0.5	-0.3	0.0	8.2	7.4
	<b>9</b>	198.3	3.1	-1.9	-0.7	0.8	0.0	199.5	199.6
	<b>10</b>	132.5	-93.4	-12.9	0.2	-1.1	0.0	26.2	25.4
	<b>11</b>	113.2	-65.2	-2.9	-0.6	-0.4	0.0	45.0	44.0
	<b>12</b>	64.8	-45.0	-3.5	-0.4	-0.2	0.0	16.3	15.7
Reverse	<b>1</b>	536.5	-151.9	-37.7	2.3	-4.8	-0.4	346.8	344.0
	<b>2</b>	172.5	-91.6	-6.9	-0.3	-0.4	0.0	74.0	73.3
	<b>3<sup>b</sup></b>	361.4	-90.3	-21.7	-0.1	-1.9	N/A	249.3	247.3
	<b>4<sup>b</sup></b>	70.0	-5.7	-8.0	-0.5	-0.4	N/A	56.2	55.3
	<b>5<sup>b</sup></b>	173.6	-36.7	-13.0	-0.4	-0.8	N/A	123.9	122.7
	<b>6<sup>b</sup></b>	120.0	-33.0	-13.4	-0.4	-0.9	N/A	73.6	72.3
	<b>7</b>	71.1	-20.6	-5.2	0.9	-1.6	0.0	45.2	44.5
	<b>8</b>	195.9	-9.4	-10.3	0.4	-1.2	-0.1	176.2	175.3
	<b>9</b>	157.5	-16.7	-3.5	0.2	-0.3	-0.2	137.2	136.9
	<b>10</b>	143.1	-52.2	-9.3	-0.3	-0.8	0.0	81.6	80.5
	<b>11</b>	173.6	-108.2	-10.0	-0.5	-0.7	0.0	55.4	54.1
	<b>12</b>	113.1	-32.1	-8.3	0.0	-0.6	0.0	72.7	72.1

<sup>a</sup>The reference values are taken from W4 theory unless otherwise indicated.<sup>38</sup> <sup>b</sup>Taken from W3.2 theory.<sup>38</sup> <sup>c</sup>CCSD correlation component. <sup>d</sup>CCSD(T)-CCSD correlation component. <sup>e</sup>CCSDT-CCSD(T) correction. <sup>f</sup>CCSDTQ-CCSDT correction from W4 theory or CCSDT(Q)-CCSDT correction from W3.2 theory. <sup>g</sup>CCSDTQ5-CCSDTQ correction from W4 theory. <sup>h</sup>Valence CCSD(T)/CBS reference values from W4 or W3.2 theory. <sup>i</sup>Valence CCSDTQ5/CBS reference values from W4 theory or CCSDT(Q)/CBS reference values from W3.2 theory.

### 3.2. Basis set convergence of the CCSD(T) energy components for the DBH24 database.

Table 2 gives an overview of the basis set convergence of the SCF, CCSD, and (T) components calculated with the VnZ and A'VnZ basis sets ( $n = \text{D, T, and Q}$ ). The RMSDs are also displayed in Figure 1. As expected, diffuse functions are critical for the basis set convergence of the SCF component. The VDZ, VTZ, and VQZ basis sets result in RMSDs of 19.8, 10.1, and 6.0 kJ mol<sup>-1</sup>,

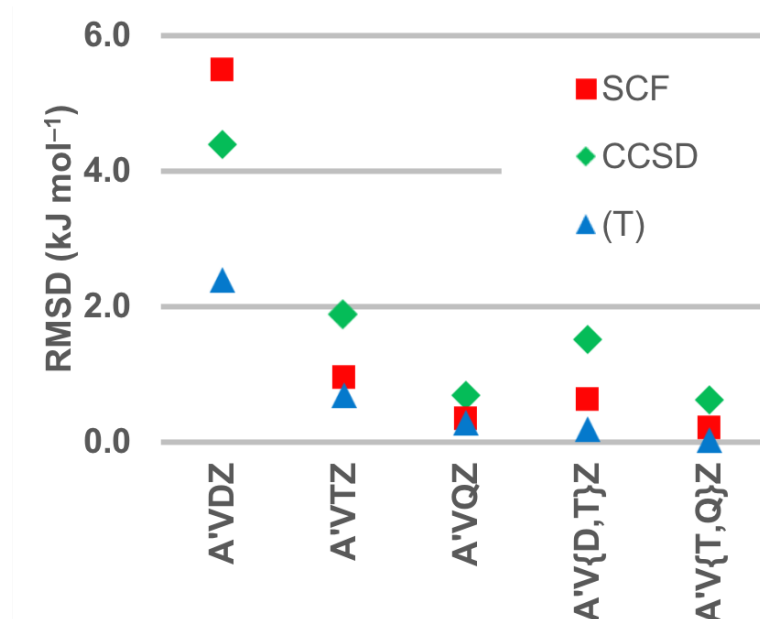
respectively and basis set extrapolations do not significantly improve the performance. Addition of diffuse functions to each of these basis sets reduces the RMSDs by about an order of magnitude. In particular, we obtain the following RMSDs 5.5 (A'VDZ), 0.9 (A'VTZ), and 0.3 (A'VQZ) kJ mol<sup>-1</sup>. Thus, the A'VTZ basis set is the smallest basis set that results in an RMSD below the 1 kJ mol<sup>-1</sup> mark. Two-point basis set extrapolations further reduce these RMSDs by about 30%, namely we obtain RMSDs of 0.6 (A'V{D,T}Z) and 0.2 (A'V{T,Q}Z) kJ mol<sup>-1</sup>. Another advantage of the basis set extrapolations is that they result in near-zero mean signed deviations (MSDs) indicating there is no systematic bias towards underestimation or overestimation of the reaction barrier heights. In contrast, all the individual basis sets tend to systematically underestimate the reaction barrier heights.



**Table 2.** Basis set convergence of the SCF, CCSD, and (T) components of the reaction barrier heights in the DBH24 database. Error statistics are calculated relative to the reference SCF, CCSD, and (T) components from W4 and W3.2 theories listed in Table 1 (in kJ mol<sup>-1</sup>).<sup>a</sup>

		RMSD	MAD	MSD
SCF	VDZ	19.8	11.5	-7.8
	VTZ	10.1	5.0	-3.1
	VQZ	6.0	2.7	-1.8
	V{D,T}Z	8.7	4.2	-2.4
	V{T,Q}Z	4.8	2.0	-1.4
	A'VDZ	5.5	4.3	-2.7
	A'VTZ	0.9	0.8	-0.3
	A'VQZ	0.3	0.2	-0.1
	A'V{D,T}Z	0.6	0.5	0.0
	A'V{T,Q}Z	0.2	0.2	0.0
CCSD	VDZ	8.0	6.6	5.0
	VTZ	4.4	3.3	1.6
	VQZ	2.7	1.8	0.3
	V{D,T}Z	4.1	2.8	0.2
	V{T,Q}Z	2.1	1.1	-0.6
	A'VDZ	4.4	3.4	1.5
	A'VTZ	1.9	1.6	0.1
	A'VQZ	0.7	0.6	0.0
	A'V{D,T}Z	1.5	1.3	-0.4
	A'V{T,Q}Z	0.6	0.5	-0.1
(T)	VDZ	3.7	2.9	2.9
	VTZ	1.6	1.2	0.9
	VQZ	1.0	0.7	0.2
	V{D,T}Z	1.1	0.7	0.1
	V{T,Q}Z	1.0	0.4	-0.3
	A'VDZ	2.4	1.9	1.9
	A'VTZ	0.7	0.5	0.5
	A'VQZ	0.3	0.2	0.2
	A'V{D,T}Z	0.2	0.2	0.0
	A'V{T,Q}Z	0.0	0.0	0.0
CCSD(T)	VDZ	22.6	15.6	0.1
	VTZ	14.1	8.6	-0.5
	VQZ	9.3	4.9	-1.3
	V{D,T}Z	13.1	7.3	-2.1
	V{T,Q}Z	7.8	3.3	-2.4
	A'VDZ	7.8	6.3	0.7
	A'VTZ	2.7	2.3	0.3
	A'VQZ	1.0	0.8	0.1
	A'V{D,T}Z	1.9	1.6	-0.5
	A'V{T,Q}Z	0.6	0.5	-0.1

<sup>a</sup>RMSD = root mean square deviation, MAD = mean absolute deviation, MSD = mean signed deviation.



**Figure 1.** Root mean square deviations (RMSDs in  $\text{kJ mol}^{-1}$ ) for the SCF, CCSD, and (T) components of the barrier heights in the DBH24 database calculated with the  $A'V_nZ$  basis sets ( $n = D, T$ , and  $Q$ ) (RMSDs are taken from Table 2). Error statistics are calculated relative to the reference SCF, CCSD, and (T) components from W4 and W3.2 theories listed in Table 1.

Let us move to the CCSD correlation component (Table 2 and Figure 1). Similar to the SCF component, the VDZ, VTZ, and VQZ basis sets result in relatively large RMSDs of 8.0, 4.4, and  $2.7 \text{ kJ mol}^{-1}$ , respectively, deeming them inadequate for the calculation of the CCSD correlation component. The addition of diffuse functions cuts these RMSDs by about 50–75%. In particular, we obtain RMSDs of 4.4 ( $A'VDZ$ ), 1.9 ( $A'VTZ$ ), and 0.7 ( $A'VQZ$ )  $\text{kJ mol}^{-1}$ . Thus, the  $A'VQZ$  is the smallest basis set that results in an RMSD below the  $1 \text{ kJ mol}^{-1}$  mark. The  $A'V\{D,T\}Z$  extrapolation results in an RMSD of  $1.5 \text{ kJ mol}^{-1}$ , i.e., it reduces the RMSD for the  $A'VTZ$  basis set by about 20%. The  $A'V\{T,Q\}Z$  extrapolation results in an even smaller improvement of about 10% over the  $A'VQZ$  basis set.

The (T) correlation component converges faster to the basis set limit than the CCSD component. However, regular (non-augmented) basis sets are still not recommended. The RMSDs for the augmented basis sets are 2.4 ( $A'VDZ$ ), 0.7 ( $A'VTZ$ ), and 0.3 ( $A'VQZ$ )  $\text{kJ mol}^{-1}$ .

Here, the A'V{D,T}Z extrapolation results in an RMSD of 0.2 kJ mol<sup>-1</sup>, i.e., it provides a significant improvement of about 70% over the A'VTZ basis set. The A'V{T,Q}Z extrapolation is practically at the CBS limit with a near-zero RMSD of 0.03 kJ mol<sup>-1</sup>.

Finally, it is of interest to consider the CCSD(T) energy as a whole. As expected from the above results the regular (non-augmented) basis sets result in unacceptably large RMSDs. The A'V{D,T}Z extrapolation results in an RMSD of 1.9 kJ mol<sup>-1</sup>, which is significantly lower than that obtained for the A'VTZ basis set (2.7 kJ mol<sup>-1</sup>). The A'V{T,Q}Z extrapolation results in an RMSD of 0.6 kJ mol<sup>-1</sup>. However, a computationally cost-effective W1-type approach,<sup>71,72</sup> in which the SCF and CCSD components are extrapolated with the A'V{T,Q}Z basis sets and the (T) component with the A'V{D,T}Z basis sets results in a similar RMSD of 0.7 kJ mol<sup>-1</sup>.

**3.3. Basis set convergence of post-CCSD(T) contributions for the DBH24 database.** Table 3 gives an overview of the basis set convergence of the higher-order triples (T–(T)) relative to reference values from W4 theory. Inspection of Table 1 reveals that the reference T–(T)/V{D,T}Z component mostly reduce the reaction barrier heights by up to 0.7 kJ mol<sup>-1</sup>. Nevertheless, there are a few exceptions in which it increases the reaction barrier heights, most notably by +2.3 and +0.9 kJ mol<sup>-1</sup> in the reverse barrier heights for reactions **1** and **7**, respectively. The VDZ basis set systematically underestimates the reference values as indicated by MSD = –MAD (Table 3). Overall the VDZ basis set result in an RMSD of 0.5 kJ mol<sup>-1</sup>. Interestingly, removing the d functions from the VDZ basis set (i.e., the VDZ(p) basis set) results in smaller underestimations and hence a slightly smaller RMSD of 0.4 kJ mol<sup>-1</sup>. The VTZ basis set still systematically underestimates the reference reaction barrier heights but results in a much smaller RMSD of 0.1 kJ mol<sup>-1</sup>. Replacing the 2d1f functions with the d function from the VDZ basis set (i.e., the VTZ(1d) basis set) results in a larger RMSD of 0.3 kJ mol<sup>-1</sup>. The V{D,T(1d)}Z basis set extrapolation, however, leads to a respectable RMSD of 0.2 kJ mol<sup>-1</sup>. Therefore this

cost-effective extrapolation from W3.2lite theory<sup>51</sup> is recommended in cases where the V{D,T}Z extrapolation is not a viable option (*vide infra*).

**Table 3.** Basis set convergence of post-CCSD(T) components of the reaction barrier heights in the DBH24 database. The reference T–(T)/CBS and T<sub>4</sub>/CBS contributions to the reaction barrier heights are listed in Table 1 (in kJ mol<sup>–1</sup>).<sup>a</sup>

		RMSD	MAD	MSD
T–(T)	VDZ(p)	0.4	0.3	-0.1
	VDZ	0.5	0.3	-0.3
	VTZ(1d)	0.3	0.2	-0.2
	VTZ	0.1	0.1	-0.1
	V{D,T(1d)}Z	0.2	0.2	-0.1
(Q)–T	VDZ(p)	0.7	0.6	0.3
	VDZ	0.4	0.3	0.1
(Q)–(T)	VDZ(p)	0.6	0.5	0.2
	VDZ	0.5	0.4	-0.2
	T–(T)/VDZ + (Q)/VDZ(p)	0.6	0.4	0.0
	T–(T)/V{D,T(1d)}Z + (Q)/VDZ(p)	0.7	0.5	0.2
	T–(T)/V{D,T(1d)}Z + (Q)/VDZ	0.5	0.3	0.0

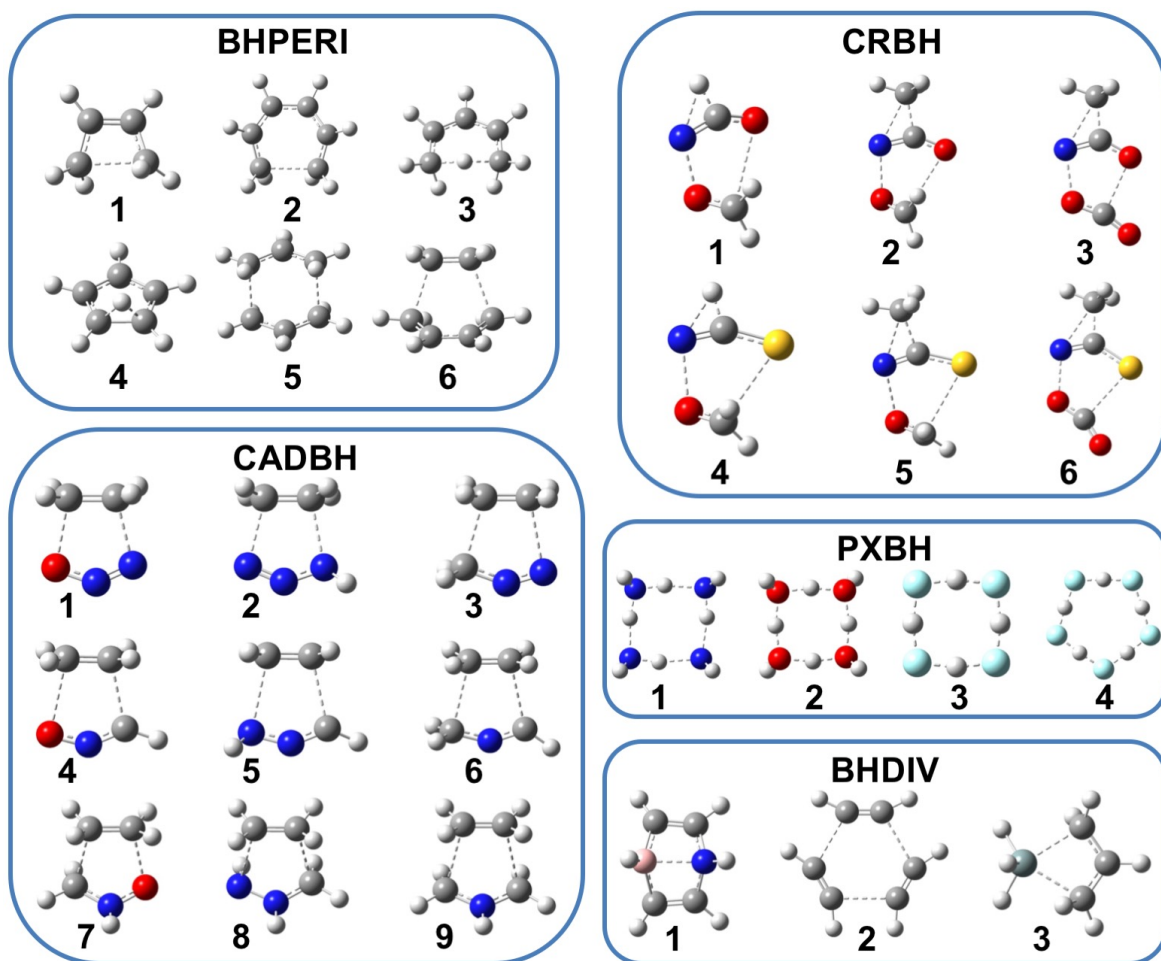
<sup>a</sup>RMSD = root mean square deviation, MAD = mean absolute deviation, MSD = mean signed deviation.

The connected quadruple excitations from W3.2 and W4 theories are fairly significant and, with only one exception, they systematically reduce the reaction barrier heights (Table 1). In particular, they reduce the barrier heights by amounts ranging from 0.2 to 4.8 kJ mol<sup>–1</sup>, where in 14 cases the reductions exceed 0.5 kJ mol<sup>–1</sup> and in seven of those they exceed 1 kJ mol<sup>–1</sup>. Relative to the T<sub>4</sub> reference values from W3.2 and W4 theories, the (Q)/VDZ level of theory results in a respectable RMSD of 0.4 kJ mol<sup>–1</sup>. Removing the d function from the VDZ basis set (i.e., the VDZ(p) basis set) results in a significant increase in the RMSD to 0.7 kJ mol<sup>–1</sup>.

Finally, it is worthwhile examining the basis set convergence of the higher-order triples T–(T) and connected quadruple (Q) excitations as a whole. Calculating the (Q)–(T) contribution with the VDZ basis set results in an RMSD of 0.5 kJ mol<sup>–1</sup>. This RMSD is increased by merely

0.1 kJ mol<sup>-1</sup> (to 0.6 kJ mol<sup>-1</sup>) with the VDZ(p) basis set. However, whilst the VDZ tends to systematically underestimate the reaction barrier heights the VDZ(p) basis set tends to systematically overestimate them (Table 3).

**3.4 Moving to larger and more complex TSs in the BH28 database.** In the previous sections we examined the basis sets convergence of the reaction barrier heights in the DBH24 database, which consists of four subsets: hydrogen transfer, heavy-atom transfer, bimolecular nucleophilic substitution, and unimolecular/recombination reactions (these TSs are relatively small and involve 1–3 non-hydrogen atoms). It is of interest to examine the basis set convergence of CCSD(T) and post-CCSD(T) components of reaction barrier heights involving larger and more complex TSs. Here we construct a broad and diverse database of barrier heights involving larger TSs with 4–7 non-hydrogen atoms. This set includes reaction barrier heights of pericyclic (BHPERI),<sup>73,74</sup> bipolar cycloaddition (CADBH),<sup>74,75</sup> cycloreversion (CRBH),<sup>76</sup> multiple proton exchange (PXBH),<sup>77</sup> and other reactions (BHDIV).<sup>78</sup> This collection of 28 reaction barrier heights will be referred to as the BH28 database and the 28 transition structures are shown in Figure 2.



**Figure 2.** Overview of the transition structures in the BH28 database containing 4–7 non-hydrogen atoms. Bonds being broken or formed are represented by dashed lines. Atomic color scheme: H, white; B, pink; C, light gray; N, blue; O, red; F, turquoise; Si, dark gray; S, yellow.

**3.5. Reference reaction barrier heights in the BH28 database.** We use W3lite-F12 theory<sup>51,52</sup> for obtaining the reference reaction barrier heights in the BH28 database at the CCSDT(Q)/CBS level of theory. It is important to mention that W3.2lite theory attains excellent performance relative to the W4/W3.2 reaction barrier heights in the DBH24 database. Namely, relative to the W4/W3.2 reference values, W3.2lite theory results in an overall MAD and RMSD of 0.6 and 0.9 kJ mol<sup>-1</sup>. Relative to the 16 reaction barrier heights for which we have CCSDTQ5/CBS reference values, W3.2lite theory results in similar MAD and RMSD values of 0.5 and 0.8 kJ mol<sup>-1</sup>, respectively. These results indicate that W3lite-F12 theory is an appropriate, yet cost-effective,

composite method for the calculation of benchmark reference reaction barrier heights. The component breakdown of the W3lite-F12 reference values is given in Table 4.

**Table 4.** Component breakdown of the W3lite-F12 benchmark reaction barrier heights in the BH28 database.

Database	TS <sup>a</sup>	SCF <sup>b</sup>	$\Delta\text{CCSD}^c$	$\Delta(\text{T})^d$	$\Delta\text{T}-(\text{T})^e$	$\Delta(\text{Q})^f$	$\Delta(\text{Q})-(\text{T})^g$	$E_e^{\ddagger h}$	$E_e^{\ddagger i}$
<b>PXBH</b>	<b>1</b>	292.2	-72.3	-16.7	0.7	-1.2	-0.5	203.1	202.6
	<b>2</b>	194.9	-67.8	-15.0	0.8	-1.2	-0.4	112.1	111.7
	<b>3</b>	116.8	-45.7	-10.3	0.4	-0.6	-0.2	60.8	60.6
	<b>4</b>	119.3	-48.0	-10.8	0.4	-0.6	-0.2	60.5	60.3
<b>BHPERI</b>	<b>1</b>	186.8	-26.1	-14.3	0.6	-1.3	-0.7	146.4	145.7
	<b>2</b>	196.9	-51.5	-17.3	2.1	-1.5	0.6	128.1	128.7
	<b>3</b>	245.7	-61.7	-17.9	1.7	-1.7	0.0	166.1	166.1
	<b>4</b>	150.5	-24.2	-7.7	1.0	-0.4	0.6	118.6	119.2
	<b>5</b>	243.0	-64.1	-25.4	2.7	-2.4	0.3	153.6	153.8
	<b>6</b>	205.3	-87.7	-25.1	2.6	-2.2	0.4	92.5	92.9
<b>CADBH</b>	<b>1</b>	224.9	-84.1	-27.4	3.8	-3.8	0.0	113.3	113.3
	<b>2</b>	188.0	-80.3	-25.7	3.8	-3.4	0.4	82.0	82.5
	<b>3</b>	154.2	-76.4	-21.9	3.1	-2.8	0.3	55.9	56.2
	<b>4</b>	153.3	-79.3	-26.3	3.3	-4.3	-1.0	47.6	46.6
	<b>5</b>	109.0	-63.9	-18.7	3.1	-2.7	0.4	26.3	26.7
	<b>6</b>	104.9	-67.4	-18.4	3.1	-2.4	0.7	19.0	19.8
	<b>7</b>	140.0	-67.5	-19.0	2.9	-2.0	0.9	53.6	54.4
	<b>8</b>	105.6	-65.5	-16.3	3.0	-1.7	1.3	23.8	25.0
	<b>9</b>	64.5	-50.8	-12.6	2.4	-1.4	1.0	1.1	2.2
<b>CRBH</b>	<b>1</b>	184.6	22.6	-10.6	-2.9	-1.7	-4.6	196.6	192.1
	<b>2</b>	196.4	26.1	-11.2	-2.4	-1.7	-4.1	211.3	207.2
	<b>3</b>	157.5	34.7	-9.3	-2.9	-1.6	-4.5	182.9	178.5
	<b>4</b>	190.6	18.5	-15.8	-2.1	-4.6	-6.7	193.3	186.6
	<b>5</b>	197.4	30.2	-11.7	-2.1	-2.9	-5.0	215.8	210.8
	<b>6</b>	150.4	40.0	-8.2	-2.9	-2.2	-5.1	182.2	177.1
<b>BHDIV</b>	<b>1</b>	260.6	-24.0	0.2	0.1	0.2	0.3	236.8	237.0
	<b>2</b>	338.5	-100.3	-28.9	3.1	-3.7	-0.6	209.2	208.6
	<b>3</b>	338.2	-49.3	-14.9	0.3	-1.5	-1.2	274.0	272.8

<sup>a</sup>For the TSs see Fig. 2. <sup>b</sup>HF\*/VQZ-F12 (including a CABS correction). <sup>c</sup>CCSD/V{T,Q}Z-F12. <sup>d</sup>(T)/VQZ-F12. <sup>e</sup>T-(T)/V{D,T(1d)}Z. <sup>f</sup>(Q)/VDZ. <sup>g</sup>Overall CCSDT(Q)-CCSD(T) contribution. <sup>h</sup>Valence, non-relativistic, vibrationless CCSD(T)/CBS reaction barrier heights (for all-electron and relativistic values see Table S1 of the Supporting Information). <sup>i</sup>Valence, non-relativistic, vibrationless CCSDT(Q)/CBS reaction barrier heights (for all-electron and relativistic values see Table S1 of the Supporting Information).

The Hartree–Fock reaction barrier heights at the CBS limit spread over a wide range, namely they range between 64.5 (**9**, CADBH) to 338.5 (**2**, BHDIV)  $\text{kJ mol}^{-1}$ . In nearly all cases, the HF/CBS reaction barrier heights overestimate the CCSDT(Q)/CBS values. In particular, these overestimations range between 22.3 (**1**, BHDIV) to 128.9 (**2**, BHDIV)  $\text{kJ mol}^{-1}$ . The CRBH dataset is an exception, where the HF/CBS reaction barrier heights tend to underestimate the CCSDT(Q)/CBS values by up to 30  $\text{kJ mol}^{-1}$  (Table 4).

With the exception of the CRBH dataset, the CCSD correlation component reduces the reaction barrier heights by 24.0 (**1**, BHDIV) to 100.3 (**2**, BHDIV)  $\text{kJ mol}^{-1}$ . For the CRBH dataset, however, the CCSD/CBS component systematically increases the reaction barrier heights by 18.5 (**4**, CRBH) to 40.0 (**6**, CRBH)  $\text{kJ mol}^{-1}$ . This reverse trend for the CRBH database may be a result of the difficult fragmentation TSs involved in this subset (Figure 2). It should be noted, however, that the same behavior is observed for the forward barrier heights of reactions **5** and **9** in the DBH24 database, albeit to a much smaller extent. Namely, the CCSD/CBS component increases these reaction barrier heights by 1.4 and 3.1  $\text{kJ mol}^{-1}$ , respectively (Table 1).

The (T)/CBS correlation contribution reduces the reaction barrier heights across the board by amounts ranging from 7.7 (**4**, BHPERI) to 28.9 (**2**, BHDIV)  $\text{kJ mol}^{-1}$ . The one exception, is reaction **1** in the BHDIV dataset in which the (T) correlation component is essentially nil (namely, +0.2  $\text{kJ mol}^{-1}$ ).

The higher-order triples (T–(T)) component ranges between 0.1 (**1**, BHDIV) and 3.8 (**1** and **2**, CADBH)  $\text{kJ mol}^{-1}$  for all the datasets except CRBH. Particularly large T–(T) contributions, ranging between 2.4–3.8  $\text{kJ mol}^{-1}$ , are obtained for the CADBH dataset. Whilst relatively small T–(T) contributions of 0.4–0.8  $\text{kJ mol}^{-1}$  are obtained for the proton transfers in the PXBH dataset. Notably, with the exception of the CRBH dataset, the T–(T) component is positive in all cases. For the CRBH dataset, on the other hand, the T–(T) component is negative



and relatively large. In particular, it ranges between  $-2.1$  (**4** and **5**, CRBH) and  $-2.9$  (**1**, **3**, and **6**, CRBH)  $\text{kJ mol}^{-1}$ .

The (Q) component is negative for all the reaction barrier heights, ranging from  $-0.4$  (**4**, BHPERI) to  $-4.6$  (**4**, CRBH)  $\text{kJ mol}^{-1}$ . The one exception, is reaction **1** in the BHDIV dataset for which the (Q) correlation component is essentially nil (namely,  $+0.2 \text{ kJ mol}^{-1}$ ). Particularly large contributions, of  $4\text{--}5 \text{ kJ mol}^{-1}$  are obtained for reactions **2** (BHDIV), **4** (CRBH), and **1** and **4** (CADBH). Whilst significantly smaller (Q) contributions of up to  $\sim 1 \text{ kJ mol}^{-1}$  are obtained for all the reactions in the PXBH dataset.

**3.6 Basis set convergence of the CCSD correlation energy for the BH28 database.** Before proceeding to a discussion of the basis set convergence of the CCSD correlation component, we note that a detailed discussion of the basis set of the SCF component is provided in the Supporting Information. Table 5 gives an overview of the basis set convergence of the CCSD correlation component of the reaction barrier heights in the BH28 database. Calculating the CCSD correlation energy with the A'VDZ basis set results in an overall RMSD of  $6.2 \text{ kJ mol}^{-1}$ . For the individual subsets we obtain RMSDs of  $2\text{--}4 \text{ kJ mol}^{-1}$  apart from the CRBH dataset for which a significantly larger RMSD of  $12.3 \text{ kJ mol}^{-1}$  is obtained. Thus, it is clear that the basis set dependency of the CCSD correlation energy is much more pronounced for the CRBH dataset. Using the A'VTZ basis set reduces the overall RMSD by  $\sim 50\%$  to  $2.7 \text{ kJ mol}^{-1}$ , with an RMSD of  $4.4 \text{ kJ mol}^{-1}$  for the CRBH dataset and RMSDs of  $1\text{--}2 \text{ kJ mol}^{-1}$  for the other datasets. We note that for the CRBH dataset, extrapolating the CCSD correlation component from the A'VDZ and A'VTZ basis sets significantly improves performance over the A'VTZ basis set, i.e., the RMSD is reduced from  $4.4$  to  $1.2 \text{ kJ mol}^{-1}$ . However, for the other subsets the A'V{D,T}Z extrapolation results in little or no improvement over the A'VTZ results (Table 5). The A'VQZ basis set results

in an overall RMSD of 0.9 kJ mol<sup>-1</sup>, where CRBH is the only dataset with an RMSD larger than 1 kJ mol<sup>-1</sup>.

**Table 5.** Basis set convergence of the CCSD correlation component for the reaction barrier heights in the BH28 database. The reference CCSD/V{T,Q}Z-F12 correlation contributions to the reaction barrier heights from W2-F12 theory are listed in Table 4 (in kJ mol<sup>-1</sup>).<sup>a</sup>

		VDZ	VTZ	VQZ	V{D,T}Z	A'VDZ	A'VTZ	A'VQZ	A'V{D,T}Z
RMSD	PXBH	2.5	3.0	1.1	3.2	1.6	1.4	0.6	1.5
	BHPERI	5.5	1.6	0.6	1.4	3.9	2.0	0.7	1.9
	CADBH	9.6	3.0	1.6	0.6	2.6	2.2	0.5	2.3
	CRBH	7.8	3.5	1.7	2.4	12.3	4.4	1.6	1.2
	BHDIV	3.7	0.5	0.3	1.0	2.2	1.5	0.5	2.0
	All	7.2	2.7	1.3	1.8	6.2	2.7	0.9	1.9
MAD	PXBH	2.3	2.7	1.0	2.9	1.4	1.3	0.5	1.3
	BHPERI	4.8	1.4	0.5	1.2	3.0	1.7	0.6	1.6
	CADBH	9.3	2.9	1.5	0.5	2.2	2.2	0.5	2.2
	CRBH	7.2	3.3	1.7	1.8	12.1	4.4	1.6	1.1
	BHDIV	3.2	0.4	0.3	0.8	2.1	1.3	0.4	2.0
	All	6.2	2.4	1.1	1.3	4.4	2.3	0.8	1.7
MSD	PXBH	-1.5	-2.0	-0.8	-2.3	-0.3	-1.0	-0.4	-1.2
	BHPERI	3.3	0.2	0.2	-1.1	-1.0	-1.4	-0.4	-1.6
	CADBH	9.3	2.9	1.5	0.2	-2.2	-2.2	-0.5	-2.2
	CRBH	-7.2	-3.3	-1.7	-1.7	-12.1	-4.4	-1.6	-1.1
	BHDIV	3.2	0.4	0.3	-0.8	0.4	-1.3	-0.4	-2.0
	All	2.3	0.0	0.1	-0.9	-3.5	-2.2	-0.7	-1.7

<sup>a</sup>RMSD = root mean square deviation, MAD = mean absolute deviation, MSD = mean signed deviation.

As discussed in Section 3.5, an intriguing feature of the barrier heights of the CRBH dataset is that the CCSD/CBS correlation component is positive rather than negative, as is the case for all the other subsets (Table 4). The CCSD/A'VDZ systematically and severely underestimates the CCSD/CBS values, with MAD = -MSD = 12.1 kJ mol<sup>-1</sup>. Interestingly, using the VDZ basis set results in a less pronounced underestimations and hence better performance with an RMSD of 7.8 kJ mol<sup>-1</sup> (cf. an RMSD of 12.3 kJ mol<sup>-1</sup> for A'VDZ). For the other datasets, the RMSDs for the VDZ basis set is larger than those for the A'VDZ basis set by 0.9 (PXBH),

1.5 (BHDIV), 1.7 (BHPERI), and 7.0 (CADBH)  $\text{kJ mol}^{-1}$ . As expected, the addition of diffuse functions is very important for the barrier heights in the CADBH database, however, for the other datasets the reductions in RMSD range between 0.8 – 1.6  $\text{kJ mol}^{-1}$ .

**3.7 Basis set convergence of the (T) correlation energy for the BH28 database.** Table 6 gives an overview of the basis set convergence of the (T) correlation component of the reaction barrier heights in the BH28 database. The (T) component converges fairly smoothly and rapidly to the basis set limit for the reaction barrier heights in the PXBH, BHPERI, CADBH, and BHDIV databases. The RMSDs for these databases are reduced from 2.1–2.4 ( $\text{A}'\text{VDZ}$ ), to 0.7–0.8 ( $\text{A}'\text{VTZ}$ ), and 0.2–0.4 ( $\text{A}'\text{VQZ}$ )  $\text{kJ mol}^{-1}$ . Consequently, the  $\text{A}'\text{V}\{\text{D,T}\}\text{Z}$  extrapolation is an effective approach in reaching the (T)/CBS limit, resulting in smaller RMSDs than those for the  $\text{A}'\text{VQZ}$  basis set. In all of these cases the smaller basis sets systematically overestimate the CBS values as indicated by  $\text{MSD} \approx \text{MAD}$ . For the CRBH database, on the other hand, the  $\text{A}'\text{VDZ}$  basis tends to systematically underestimate the reaction barrier heights, whilst the  $\text{A}'\text{VTZ}$  basis set tends to systematically overestimate them (Table 6). Thus, the barrier heights in the CRBH database exhibits an erratic basis set convergence with RMSDs of 0.4 ( $\text{A}'\text{VDZ}$ ), 0.5 ( $\text{A}'\text{VTZ}$ ), and 0.8 ( $\text{A}'\text{VQZ}$ )  $\text{kJ mol}^{-1}$ .

**Table 6.** Basis set convergence of the (T) correlation component for the reaction barrier heights in the BH28 database. The reference (T)/VQZ-F12 correlation contributions to the reaction barrier heights from W2-F12 theory are listed in Table 4 (in  $\text{kJ mol}^{-1}$ ).<sup>a</sup>

		VDZ	VTZ	VQZ	V{D,T}Z	A'VDZ	A'VTZ	A'VQZ	A'V{D,T}Z
RMSD	PXBH	3.5	0.8	0.4	0.6	2.4	0.8	0.4	0.1
	BHPERI	3.4	1.1	0.5	0.2	2.2	0.7	0.4	0.2
	CADBH	4.9	1.7	0.8	0.4	2.1	0.8	0.4	0.3
	CRBH	0.4	1.3	1.0	1.7	0.4	0.5	0.8	0.8
	BHDIV	3.4	1.2	0.4	0.3	2.4	0.7	0.2	0.1
	All	3.6	1.3	0.7	0.8	2.0	0.7	0.5	0.4
MAD	PXBH	3.5	0.7	0.3	0.5	2.4	0.8	0.4	0.1
	BHPERI	3.2	1.0	0.5	0.2	2.1	0.7	0.4	0.2
	CADBH	4.8	1.6	0.7	0.3	2.1	0.8	0.4	0.3
	CRBH	0.3	1.3	1.0	1.7	0.3	0.5	0.8	0.8
	BHDIV	2.9	0.9	0.3	0.2	2.0	0.6	0.2	0.1
	All	3.1	1.2	0.6	0.6	1.7	0.7	0.4	0.3
MSD	PXBH	3.5	0.7	0.3	-0.5	2.4	0.8	0.4	0.1
	BHPERI	3.2	1.0	0.5	0.1	2.1	0.7	0.4	0.1
	CADBH	4.8	1.6	0.7	0.3	2.1	0.8	0.4	0.3
	CRBH	0.2	1.3	1.0	1.7	-0.3	0.5	0.8	0.8
	BHDIV	2.9	0.9	0.3	0.1	2.0	0.6	0.1	-0.1
	All	3.1	1.2	0.6	0.4	1.6	0.7	0.4	0.3

<sup>a</sup>RMSD = root mean square deviation, MAD = mean absolute deviation, MSD = mean signed deviation.

**3.8 Basis set convergence of the CCSD(T) energy as a whole for the BH28 database.** Table 7 gives an overview of the basis set convergence of the CCSD(T) reaction barrier heights in the BH28 database. As expected, the A'VDZ basis set results in large RMSDs ranging from 4.3 (BHPERI) to 14.4 (CRBH)  $\text{kJ mol}^{-1}$ , and an overall RMSD of 10.0  $\text{kJ mol}^{-1}$ . The RMSDs for the A'VTZ are significantly smaller, ranging from 1.6 (BHDIV) to 3.7 (CRBH)  $\text{kJ mol}^{-1}$ , and an overall RMSD of 2.9  $\text{kJ mol}^{-1}$ . The A'V{D,T}Z extrapolation improves on the A'VTZ results for the CADBH and CRBH datasets, however, results in larger RMSDs for the PXBH and BHDIV datasets. Thus, basis set extrapolations involving the small A'VDZ basis set should be used with caution.

**Table 7.** Basis set convergence of the CCSD(T) method for the reaction barrier heights in the BH28 database. The reference CCSD(T)/CBS reaction barrier heights from W2-F12 theory are listed in Table 4 (in  $\text{kJ mol}^{-1}$ ).<sup>a</sup>

		VDZ	VTZ	VQZ	V{D,T}Z <sup>b</sup>	W1-type <sup>b,c</sup>	A'VDZ	A'VTZ	A'VQZ	A'V{D,T}Z <sup>b</sup>	W1-type <sup>b,c</sup>	W1-type <sup>d</sup>
RMSD	PXBH	2.7	5.6	1.5	7.1	0.3	7.7	3.4	0.6	5.5	0.5	0.3
	BHPERI	4.9	1.5	0.7	1.7	0.5	4.3	2.2	0.4	2.2	0.7	0.3
	CADBH	3.4	2.8	1.7	2.6	1.1	11.0	2.9	0.5	2.3	1.1	0.4
	CRBH	17.8	2.2	1.3	3.1	0.5	14.4	3.7	1.0	1.1	0.9	0.3
	BHDIV	5.5	1.6	0.8	1.7	0.7	6.2	1.6	0.5	2.6	0.5	0.4
	All	9.0	3.0	1.3	3.5	0.8	10.0	2.9	0.6	2.8	0.9	0.4
MAD	PXBH	2.4	4.9	1.4	6.1	0.2	6.7	2.9	0.5	4.9	0.4	0.2
	BHPERI	4.1	1.3	0.7	1.4	0.4	4.0	1.9	0.4	1.8	0.6	0.3
	CADBH	2.8	2.3	1.4	1.8	1.0	10.2	2.9	0.4	2.1	1.1	0.4
	CRBH	17.8	1.9	1.2	2.4	0.5	14.2	3.6	1.0	0.9	0.8	0.3
	BHDIV	4.9	1.2	0.7	1.5	0.6	5.8	1.5	0.4	2.5	0.4	0.2
	All	6.4	2.3	1.1	2.4	0.6	8.8	2.7	0.6	2.2	0.7	0.3
MSD	PXBH	-2.0	-4.7	-1.1	-5.9	-0.1	6.7	-2.9	-0.4	-4.9	0.4	-0.1
	BHPERI	4.1	0.8	0.6	-1.1	0.3	-2.5	-1.4	-0.2	-1.8	0.5	0.3
	CADBH	-0.3	1.4	1.1	-0.9	0.3	-10.2	-2.9	-0.4	-2.1	1.1	0.4
	CRBH	-17.8	-1.5	-1.2	2.3	0.4	-14.2	-3.6	-1.0	0.3	0.8	-0.2
	BHDIV	4.9	0.7	0.5	-1.2	0.4	-0.3	-1.5	-0.3	-2.5	0.4	0.2
	All	-2.8	-0.3	0.1	-1.0	0.3	-5.9	-2.6	-0.5	-2.0	0.7	0.1

<sup>a</sup>RMSD = root mean square deviation, MAD = mean absolute deviation, MSD = mean signed deviation. <sup>b</sup>An exponent of 5 is used for the SCF extrapolation and an exponent of 3 is used for the CCSD and (T) extrapolations. <sup>c</sup>The SCF and CCSD components are extrapolated from the A'V{T,Q}Z basis sets and the (T) component is extrapolated from the A'V{D,T}Z basis sets. <sup>d</sup>The SCF energy is calculated with the A'VQZ basis set, the CCSD correlation energy is extrapolated from the the A'V{T,Q}Z basis sets with an optimal exponent of 4.5, and the (T) component is extrapolated from the A'V{D,T}Z basis sets with an optimal exponent of 4.5.

The A'VQZ basis set results in RMSDs below  $1.0 \text{ kJ mol}^{-1}$  for all the subsets and an overall RMSD of  $0.6 \text{ kJ mol}^{-1}$  for the BH28 database. However, a computationally effective W1-type approach, in which the SCF and CCSD components are extrapolated with the A'V{T,Q}Z basis sets and the (T) component with the A'V{D,T}Z basis sets results in an RMSD of  $0.9 \text{ kJ mol}^{-1}$ . It should be pointed out that calculating the SCF with the A'VQZ basis set instead of the A'V{T,Q}Z extrapolation and using an optimal exponent of 4.5 in the CCSD and (T)

extrapolations results in a very low RMSD of merely 0.4 kJ mol<sup>-1</sup> (these results are presented in the last column of Table 7).

It is noteworthy that for two datasets (PXBH and CADBH) the overall RMSDs for the A'VDZ basis set are larger than those for the VDZ basis set (Table 7). Inspection of the error statistics for the SCF, CCSD, and (T) components reveals that this anomalous basis set convergence is a result of error compensation which occurs for the VDZ basis set but not the A'VDZ basis set. For the CADBH subset, the SCF component systematically and significantly underestimates the SCF/CBS energy as evident from MSD = -MAD = -14.4 kJ mol<sup>-1</sup> (Table S2 of the Supporting Information). On the other hand, both the CCSD and (T) correlation components systematically overestimate the CCSD/CBS and (T)/CBS components, respectively. Namely, for the CCSD correlation component MSD = MAD = 9.3 kJ mol<sup>-1</sup> (Table 5) and for the (T) correlation component MSD = MAD = 4.8 kJ mol<sup>-1</sup> (Table 6). This error compensation between the SCF and correlation components leads to an RMSD of merely 3.4 kJ mol<sup>-1</sup> for the overall CCSD(T) energy. Inspection of the MADs and MSDs for the A'VDZ basis set (Tables 5–7) reveals that, in contrast to the VDZ basis set, both the SCF and CCSD correlation components systematically underestimate the SCF/CBS and CCSD/CBS components, respectively. The (T) correlation component still overestimates the (T)/CBS component, however, the lesser degree of error compensation leads to an RMSD of 11.0 kJ mol<sup>-1</sup> for the overall CCSD(T) energy. For the PXBH subset, the SCF/VDZ and CCSD/VDZ correlation components tend to underestimate the SCF/CBS and CCSD/CBS components, respectively (Tables 5 and 6), whilst the (T)/VDZ component overestimates the (T)/CBS limit by a similar amount (Table 6). Overall, the RMSD for the CCSD(T)/VDZ is 2.7 kJ mol<sup>-1</sup>. For the A'VDZ, however, both the SCF and (T) components tend to overestimate the SCF/CBS and (T)/CBS components, respectively, whilst the CCSD correlation component does not exhibit bias towards overestimation or underestimation of

the CCSD/CBS correlation energy. Thus, the CCSD(T)/A'VDZ level of theory does not benefit from error compensation and results in an RMSD of 5.7 kJ mol<sup>-1</sup>.

**3.9 Basis set convergence of the T–(T) correlation energy for the BH28 database.** Table 8 gives an overview of the basis set convergence of the CCSDT–CCSD(T) difference for the reaction barrier heights in the BH28 database. Before examining the error statistics for the various basis sets it is worth restating that the W3lite-F12 basis-set limit values are normally positive, and range between +0.1 and +3.8 kJ mol<sup>-1</sup> (Table 4). The main exceptions to this are the reaction barrier heights in the CRBH dataset, for which the T–(T) component is negative and ranges between –2.1 and –2.9 kJ mol<sup>-1</sup>. The average magnitude of the T–(T) component for each of the subsets in the BH28 database is 0.6 (PXBH), 1.8 (BHPERI), 3.2 (CADBH), –2.6 (CRBH), and 1.2 (BHDIV) kJ mol<sup>-1</sup>, with largest T–(T) contributions of 0.8 (PXBH), 2.7 (BHPERI), 3.8 (CADBH), –2.9 (CRBH), and 3.1 (BHDIV) kJ mol<sup>-1</sup>.

**Table 8.** Basis set convergence of the CCSDT–CCSD(T) (T–(T)) component for the reaction barrier heights in the BH28 database. The reference T–(T)/V{D,T(1d)}Z reaction barrier heights from W3lite-F12 theory are listed in Table 4 (in kJ mol<sup>−1</sup>).<sup>a</sup>

		T–(T) VDZ(p)	T–(T) 1.80×VDZ(p)	T–(T) VDZ	T–(T) 1.25×VDZ	T–(T) VTZ(1d)
RMSD	PXBH	0.7	0.8	0.5	0.5	0.3
	BHPERI	1.7	1.6	0.6	0.4	0.4
	CADBH	2.1	1.3	0.8	0.3	0.5
	CRBH	1.2	1.5	0.4	0.5	0.2
	BHDIV	1.3	1.1	0.6	0.4	0.4
	All	1.6	1.3	0.6	0.4	0.4
MAD	PXBH	0.6	0.6	0.5	0.5	0.3
	BHPERI	1.6	1.5	0.5	0.3	0.3
	CADBH	2.0	1.1	0.8	0.3	0.5
	CRBH	0.8	1.4	0.2	0.5	0.2
	BHDIV	1.0	0.9	0.6	0.4	0.3
	All	1.4	1.2	0.6	0.4	0.3
MSD	PXBH	−0.6	−0.6	−0.5	−0.5	−0.3
	BHPERI	−1.6	−1.5	−0.5	−0.2	−0.3
	CADBH	−2.0	−1.1	−0.8	−0.2	−0.5
	CRBH	0.8	−0.5	0.2	−0.4	0.1
	BHDIV	−1.0	−0.9	−0.6	−0.4	−0.3
	All	−1.0	−1.0	−0.5	−0.3	−0.3

<sup>a</sup>RMSD = root mean square deviation, MAD = mean absolute deviation, MSD = mean signed deviation.

The VTZ(1d) basis set results in RMSDs ranging between 0.2 (CRBH) and 0.5 (CADBH) kJ mol<sup>−1</sup>, and an overall RMSD of 0.4 kJ mol<sup>−1</sup>. Where the T–(T)/VTZ(1d) components systematically underestimate the reference values from W3lite-F12 theory as evident from MAD = −MSD. Calculating the CCSDT energy with the VDZ basis set represents significant savings in CPU time. For example, in conjunction with the VTZ(1d) basis set, the CCSDT calculation for **TS5** in the CRBH dataset (Figure 2) ran for 6.4 days on 20 Intel Xeon E5-2670v2 cores (at 3.1 GHz) with 256 GB of RAM and 2 TB of solid-state disk, whilst with the VDZ basis set ran this calculation ran for 1.7 days on the same machine. The VDZ basis set results in more pronounced underestimations relative to the VTZ(1d) basis set and the overall RMSD for the BH28 database



is  $0.6 \text{ kJ mol}^{-1}$ . Since the VDZ basis set tends to systematically underestimate the estimated CBS values, scaling by a constant factor can be a cost-effective approach for improving performance.<sup>54,79,80</sup> Optimizing the scaling factor to minimize the RMSD over the BH28 database results in a scaling factor of 1.25 and an RMSD of  $0.4 \text{ kJ mol}^{-1}$  which is identical to that of the VTZ(1d) basis set. Thus, in cases where the CCSDT/VTZ(1d) calculation is computationally not feasible, scaling the CCSDT/VDZ–CCSD(T)/VDZ difference by 1.25 is recommended. Removing the d functions from the VDZ basis set, i.e., using the VDZ(p) basis set results in a significant deterioration in performance and severe underestimation of the T–(T) component. The overall RMSD for the VDZ(p) basis set is  $1.6 \text{ kJ mol}^{-1}$ . This RMSD is comparable to the magnitude of the T–(T) component and makes the usefulness of this calculation questionable. Furthermore, scaling by an optimal scaling factor of 1.8 does not significantly improve the performance and results in an overall RMSD of  $1.3 \text{ kJ mol}^{-1}$ .

**3.10 Basis set convergence of the (Q) correlation energy for the BH28 database.** Table 9 gives an overview of the performance of the (Q) component calculated in conjunction with the VDZ(p) and MIN basis sets. The (Q)/VDZ(p) level of theory results in a large overall RMSD of  $1.0 \text{ kJ mol}^{-1}$ . For the PXBH dataset a fairly small RMSD of  $0.3 \text{ kJ mol}^{-1}$  is obtained, however, for the other subsets significantly larger RMSDs ranging between  $0.7$  (CRBH) and  $1.2$  (CADBH) are obtained. These RMSDs should be compared to the average magnitude of the (Q) component for each of the subsets in the BH28 database. Namely,  $-0.9$  (PBX),  $-1.6$  (BHPERI),  $-2.7$  (CADBH),  $-2.5$  (CRBH), and  $-1.7$  (BHDIV)  $\text{kJ mol}^{-1}$ . Thus, the VDZ(p) basis set is clearly too small for obtaining useful estimations of the (Q) component for all the datasets apart from PBX. Inspection of the MSDs in Table 9 reveals that the VDZ(p) basis set systematically overestimates the negative (Q)/VDZ values (i.e., predicts values that are not negative enough). Thus, scaling by an optimal factor of 1.6 significantly improves performance and results in an overall RMSD of

0.5 kJ mol<sup>-1</sup>. Apart from the BHPERI dataset for which an RMSD of 0.7 kJ mol<sup>-1</sup> is obtained, the RMSDs for all the subsets are smaller or equal to 0.5 kJ mol<sup>-1</sup>.

**Table 9.** Basis set convergence of the CCSDT(Q)–CCSDT ((Q)) component for the reaction barrier heights in the BH28 database. The reference (Q)/VDZ reaction barrier heights from W3lite-F12 theory are listed in Table 4 (in kJ mol<sup>-1</sup>).<sup>a</sup>

		(Q) MIN	(Q) 1.5×MIN	(Q) VDZ(p)	(Q) 1.6×VDZ(p)
RMSD	PXBH	0.3	0.1	0.3	0.1
	BHPERI	1.1	0.8	1.1	0.7
	CADBH	1.2	0.5	1.2	0.4
	CRBH	0.5	0.6	0.7	0.5
	BHDIV	1.0	0.4	0.9	0.2
	All	1.0	0.5	1.0	0.5
MAD	PXBH	0.3	0.1	0.3	0.1
	BHPERI	1.0	0.7	1.0	0.7
	CADBH	1.1	0.3	1.1	0.3
	CRBH	0.5	0.5	0.7	0.4
	BHDIV	0.8	0.3	0.8	0.2
	All	0.8	0.4	0.9	0.4
MSD	PXBH	0.3	0.0	0.3	0.0
	BHPERI	1.0	0.7	1.0	0.7
	CADBH	1.1	0.3	1.1	0.1
	CRBH	0.5	−0.5	0.7	−0.4
	BHDIV	0.6	0.1	0.6	0.0
	All	0.8	0.2	0.8	0.1

<sup>a</sup>RMSD = root mean square deviation, MAD = mean absolute deviation, MSD = mean signed deviation.

The minimal MIN basis set gives results that are practically identical to those of the VDZ(p) basis set, with an overall RMSD of 1.0 kJ mol<sup>-1</sup>. Similarly to the VDZ(p) basis set, the systematic behaviour of the MIN basis set means that scaling by an optimal scaling factor of 1.5 dramatically improves the performance. In particular, the RMSDs for the subsets are only slightly larger than those obtained for the VDZ(p) basis set, and the overall RMSD is the same for both basis sets, namely 0.5 kJ mol<sup>-1</sup>. Thus, although results obtained with a minimal basis set should

always be treated with caution, in this case the (Q)/MIN component seems to give useful estimations.

**3.11 The (Q)–(T) component as a whole for the reaction barrier heights in the BH28 database.** It is worthwhile examining the basis set convergence of the CCSDT(Q)–CCSD(T) component as a whole. These results are presented in Table 10. We begin by noting that at the basis set limit this component can be either negative or positive and that it is normally below the  $\sim 1$  kJ mol<sup>−1</sup> (in absolute value) due to an effective cancelation between the T–(T) component (which tends to increase the reaction barrier heights) and the (Q) component (which tends to decrease them). For example, excluding the CRBH subset, the (Q)–(T) component for the barrier heights in the BH28 database ranges between  $-1.2$  (**3**, BHDIV) and  $+1.3$  (**8**, CADBH) kJ mol<sup>−1</sup> (Table 4). The CRBH subset is a notable exception, since both the T–(T) and (Q) components are negative and large. Consequently, the (Q)–(T) component ranges between  $-4.1$  (**2**) and  $-6.7$  (**4**) kJ mol<sup>−1</sup> for the CRBH dataset (Table 4).

Calculating the (Q)–(T) component with the VDZ(p) basis set results in an unacceptably large overall RMSD of 1.1 kJ mol<sup>−1</sup>. Increasing the size of the basis set for the T–(T) component to VDZ significantly improves the performance and results in an overall RMSD of 0.6 kJ mol<sup>−1</sup>. Scaling the (Q)/VDZ(p) component by 1.3 further reduces the RMSD to 0.4 kJ mol<sup>−1</sup>. Thus, this approach is recommended in cases where the use of larger basis sets is computationally too demanding.

**Table 10.** Basis set convergence of the CCSDT(Q)–CCSD(T) ((Q)–(T)) component for the reaction barrier heights in the BH28 database. The reference (Q)–(T) reaction barrier heights from W3lite-F12 theory are taken from Table 4 (in kJ mol<sup>-1</sup>).<sup>a</sup>

		(Q)–(T) VDZ(p) VDZ(p)	(Q)–(T) VDZ VDZ(p)	(Q)–(T) VDZ 1.3×VDZ(p)
	T–(T) (Q)			
RMSD	PXBH	0.4	0.2	0.4
	BHPERI	0.7	0.5	0.5
	CADBH	0.9	0.4	0.4
	CRBH	1.8	1.0	0.4
	BHDIV	0.4	0.5	0.4
	All	1.1	0.6	0.4
MAD	PXBH	0.3	0.2	0.3
	BHPERI	0.6	0.5	0.4
	CADBH	0.9	0.3	0.3
	CRBH	1.5	0.9	0.3
	BHDIV	0.4	0.5	0.3
	All	0.9	0.5	0.3
MSD	PXBH	-0.3	-0.2	-0.3
	BHPERI	-0.6	0.5	0.4
	CADBH	-0.9	0.3	0.1
	CRBH	1.5	0.9	0.1
	BHDIV	-0.4	0.1	-0.2
	All	-0.2	0.4	0.1

<sup>a</sup>RMSD = root mean square deviation, MAD = mean absolute deviation, MSD = mean signed deviation.

Finally, a word is due regarding the potential prediction of the magnitude of the post-CCSD(T) (or (Q)–(T)) contributions to the reaction barrier heights. As discussed above there is a systematic cancellation between the T–(T) and (Q) contributions to the reaction barriers. The only subset for which this cancellation does not occur is the CRBH dataset, for which both the T–(T) and (Q) contributions are negative and large (Table 4). As a result, the (Q)–(T) contribution reduces the reaction barrier heights by significant amounts of up to 6.7 kJ mol<sup>-1</sup>. Inspection of the results in Table 4 reveals that for all the subsets, apart from CRBH, the SCF and CCSD have opposite signs. However, for the CRBH dataset the SCF and CCSD correlation components are both positive and large. This anomaly has been observed here for only one subset, which is not

sufficient for making any generalizations. Nevertheless, cases where the SCF and CCSD components are both positive and large may serve as an a-priori warning indicating that post-CCSD(T) contributions may not benefit from error cancelation between the higher-order T–(T) and (Q) components.

## 4. Conclusions

We begin by evaluating the performance of W3lite-F12 relative to the W4/3.2 reference reaction barrier heights in the DBH24 database. We find that W3lite-F12 theory attains excellent performance with an RMSD and MAD of 0.9 and 0.6 kJ mol<sup>-1</sup>, respectively. We proceed to use W3lite-F12 theory for obtaining reference reaction barrier heights for a diverse set of 28 reaction barrier heights involving much larger and chemically more complex TSs (a.k.a. the BH28 database). The set of barrier heights in this database include pericyclic, bipolar cycloaddition, cycloreversion, and multiple proton transfer reactions and the TSs involve 4–7 non-hydrogen atoms. We use the W3lite-F12 CCSDT(Q)/CBS reaction barrier heights to examine the basis set convergence of CCSD(T) and of post-CCSD(T) contributions.

With regard to the basis set convergence of the CCSD(T) components, we draw the following conclusions:

- The SCF component converges fairly rapidly to the CBS limit. The A'V{D,T}Z extrapolation yields RMSDs below 1 kJ mol<sup>-1</sup> for all the subsets (e.g., pericyclic, cycloaddition, and cycloreversion reaction barrier heights) apart from multiple proton transfer reaction barrier heights. The A'VQZ basis set results in an overall RMSD of 0.3 kJ mol<sup>-1</sup>.
- Convergence of the CCSD correlation component is not uniform across the subsets. In particular, it is much slower for cycloreversion reaction barrier heights. The A'V{D,T}Z extrapolation yields an overall RMSD of 1.9 kJ mol<sup>-1</sup>. The A'VQZ basis set results in an

overall RMSD of 0.9 kJ mol<sup>-1</sup>, where CRBH is the only subset with an RMSD of over 1 kJ mol<sup>-1</sup>.

- The (T) correlation component converges fairly rapidly to the CBS limit. The A'V{D,T}Z extrapolation yields an overall RMSD of 0.4 kJ mol<sup>-1</sup>. The A'VQZ basis set results in a larger overall RMSD of 0.7 kJ mol<sup>-1</sup>.
- Diffuse functions are important for a proper description of the SCF, CCSD, and (T) correlation components. This is particularly pronounced in datasets involving polar TSs (e.g., dipolar cycloaddition reactions).
- For the calculation of reaction barrier heights at the CCSD(T)/CBS limit we recommend using a computationally economical W1-type approach: SCF/A'VQZ + CCSD/A'V{T,Q}Z + (T)/A'V{D,T}Z, in which the CCSD and (T) components are extrapolated using an optimal extrapolation exponent of 4.5. This results in a small overall RMSD of 0.4 kJ mol<sup>-1</sup> relative to CCSD(T)/CBS reference values from W2-F12 theory.

With regard to the basis set convergence of post-CCSD(T) components, we draw the following conclusions:

- The T-(T) component normally increases the reaction barrier heights, however, for the CRBH subset it systematically decreases them. The magnitude of the T-(T) component from W3lite-F12 theory for each of the subsets in the BH28 can reach up to 0.8 (PXBH), 2.7 (BHPERI), 3.8 (CADBH), -2.9 (CRBH), and 3.1 (BHDIV) kJ mol<sup>-1</sup>.
- The (Q) component from W3lite-F12 theory systematically decreases the reaction barrier heights, and can reach up to: -1.2 (PXBH), -2.4 (BHPERI), -4.3 (CADBH), -4.6 (CRBH), and -3.7 (BHDIV) kJ mol<sup>-1</sup>.
- The VDZ basis set systematically underestimates the T-(T) basis set limit values. Thus, calculating the T-(T) component with the VDZ basis set and scaling by an empirical

scaling factor of 1.25 is a cost-effective approach which results in an overall RMSD of merely 0.4 kJ mol<sup>-1</sup>. We note that the same RMSD is obtained with the computationally more demanding VTZ(1d) basis set.

- Calculating the (Q) component with the VDZ(p) basis set results in systematic overestimation of the (Q)/VDZ reference values (i.e., it predicts values that are not negative enough). Thus, scaling by an optimal factor of 1.6 significantly improves performance and results in an overall RMSD of 0.5 kJ mol<sup>-1</sup>. Apart from the BHPERI dataset for which an RMSD of 0.7 kJ mol<sup>-1</sup> is obtained, the RMSDs for all the subsets are smaller or equal to 0.5 kJ mol<sup>-1</sup>.

## Supplementary data

Relativistic, all-electron, vibrationless reference values from W3lite-F12 theory for the reaction barrier heights in the BH28 database (Table S1) and Cartesian coordinates for all the species involved in the BH28 database.

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## Graphical TOC

