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## Post-CCSD(T) corrections to bond distances and vibrational frequencies: the power of $\Lambda$

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### ABSTRACT

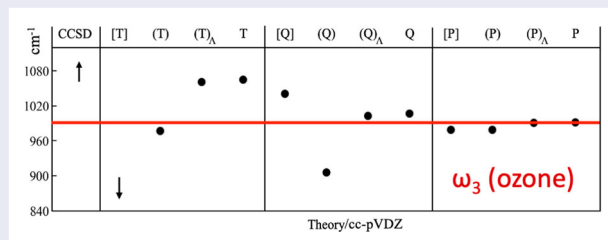
The importance of post-CCSD(T) corrections as high as CCSDTQ56 for ground-state spectroscopic constants ( $D_e$ ,  $\omega_e$ ,  $\omega_e x_e$ , and  $\alpha_e$ ) has been surveyed for a sample of two dozen mostly heavy-atom diatomics spanning a broad range of static correlation strength. While CCSD(T) is known to be an unusually felicitous ‘Pauling point’ between accuracy and computational cost, performance leaves something to be desired for molecules with strong static correlation. We find CCSDT(Q) $\Lambda$  to be the next ‘sweet spot’ up, of comparable or superior quality to the much more expensive CCSDTQ. A similar comparison applies to CCSDTQ(5) $\Lambda$  vs. CCSDTQ5, while CCSDTQ5(6) $\Lambda$  is essentially indistinguishable from CCSDTQ56. A composite of CCSD(T)-X2C/ACV5Z-X2C with [CCSDT(Q) $\Lambda$  - CCSD(T)]/cc-pVTZ or even cc-pVDZ basis sets appears highly effective for computational vibrational spectroscopy. Unlike CCSDT(Q) which breaks down for the ozone vibrational frequencies, CCSDT(Q) $\Lambda$  handles them gracefully.

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## 1. Introduction

The CCSD(T) method [1,2], coupled cluster with all single and double substitutions [3] and a quasiperturbative correction [1,2] for connected triple excitations, is also known as ‘the gold standard of quantum chemistry’ (expression first coined by T. H. Dunning, Jr. in a 2000 lecture). It is indeed a particularly felicitous compromise between accuracy and computational cost, and for most applications CCSD(T) can reliably yield chemically accurate results. However, as became apparent during high-accuracy computational thermochemistry (e.g. the Weizmann-4 [4,5] and HEAT [6–9] approaches) and computational spectroscopy studies, its excellent performance is the result of an error compensation

between neglect of higher-order triples and connected quadruples. In the presence of static correlation, this compensation becomes erratic; hence, for benchmark accuracy, one needs to go beyond CCSD(T).


Already in 2001, Musiał et al. [10] found that connected *quintuples* (!) could contribute quite nontrivially to stretching frequencies for triple bonds. This was further explored by Thøgersen and Olsen [11] and by Ruden et al. [12].

Cortez et al. [13] considered the vibrational spectrum of water, and found: that CCSD(T) was in error by just a few  $\text{cm}^{-1}$ ; that CCSDT (coupled cluster with all single, double, and triple substitutions) did not improve on this; and that CCSDT(Q) (i.e. CCSDT with

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This paper is dedicated to the memory of Dr. Timothy J. Lee (1960–2022).

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a quasiperturbative correction for connected quadruples [14]) approached the full CI limit to better than  $1 \text{ cm}^{-1}$ . (See also Kállay and Gauss [15].) These observations are consistent with Ref. [16] which defines the HFREQ27 vibrational frequencies benchmark, where CCSD(T) at the basis set limit was found to have an RMSD of  $4.6 \text{ cm}^{-1}$ . The molecules in HFREQ27 are a mix of heavy-atom and hydrogen-containing diatomics with small polyatomics, excluding cases known to exhibit strong static correlation.

In 2010, Karton and Martin [17] investigated the application of the W4 composite scheme [4] to spectroscopic constants (by finite difference of pointwise W4 energies). W4 contains terms through CCSDTQ5 (coupled cluster with all connected single through quintuple substitutions, a.k.a. CCSDTQP for ‘pentuple’ excitations<sup>1</sup>), albeit in progressively smaller basis sets as the substitution level increases. The importance of each term for frequencies was tested in that paper through truncation: the authors found that stopping at CCSD(T) caused an RMS error of just  $5 \text{ cm}^{-1}$  for diatomic hydride stretching frequencies, but  $11 \text{ cm}^{-1}$  for nonhydrides. CCSDT yielded an improvement to  $3 \text{ cm}^{-1}$  for hydrides but a deterioration to  $15 \text{ cm}^{-1}$  for nonhydrides, while truncation at CCSDTQ (i.e. only omitting the CCSDTQ5 step) brought down errors drastically to  $0.6 \text{ cm}^{-1}$  for hydrides and  $2.4 \text{ cm}^{-1}$  for nonhydrides. The cases where the quintuples contributions were significant all involve multiple bonds, but the converse is not necessarily true.

It was thus shown once again that CCSD(T) is a Pauling point or, if the reader likes, a ‘sweet spot’ between accuracy and computational cost. Prospects for going much beyond that in accuracy, on even a semi-routine basis, seem fairly bleak given the daunting  $n^4N^6$  computational cost scaling of CCSDTQ (where  $n$  represents the number of electrons correlated and  $N$  the size of the basis set).

In the context of a computational thermochemistry study reconsidering both the W4-11 thermochemistry benchmark [18,19] and W4 theory itself [E. Semidalas, A. Karton, and J. M. L. Martin, to be published] so-called lambda coupled cluster methods [20–23] seemed to show promise (see also Refs. [24,25]). However, we concluded that the  $n$ -particle space convergence of properties other than equilibrium thermochemistry, such as spectroscopic constants, might shed more light on the problem.

We present such a study here, and shall show that there is another ‘sweet spot’ beyond CCSD(T), namely CCSDT(Q)<sub>Λ</sub>. In addition, we shall demonstrate that CCSDTQ(5)<sub>Λ</sub> can essentially be considered full CI quality for most purposes.

In addition, as a polyatomic ‘proof of principle’, we will consider the vexing problem of the ozone vibrational frequencies. Stanton, Magers et al. [26,27] found in 1989 that the asymmetric stretch in particular is inordinately sensitive to the treatment of triple excitations. This is caused primarily by a low-lying  $[\dots](4b_2)^2(6a_1)^2(2b_1)^2$  configuration, with redistribution within the  $\pi$  space a close second. Refs. [26,27] considered quasiperturbative approaches such as CCSD[T] as well as approximate iterative approaches such as CCSDT-1 and CCSDT-2 [28]. Watts et al. [29] upgraded this to full CCSDT, and found that the asymmetric stretch differed by  $100 \text{ cm}^{-1}$  from CCSDT-2 and by  $41 \text{ cm}^{-1}$  from the more advanced CCSDT-3; in contrast, CCSD(T) (first reported in the original paper [1] defining this method) lay  $100 \text{ cm}^{-1}$  below CCSDT, while the more approximate CCSD[T] yielded an unphysical symmetry breaking – making this method worse than omitting triples altogether (in this high-static-correlation regime).

Watts et al. [29] also suggested that connected quadruples,  $T_4$ , might have a significant impact on the final result. This was first considered by Kucharski and Bartlett [30] using the reduced-cost, factorised CCSDT(Q<sub>f</sub>) approach. They found that the effect of  $T_4$  on the total was highly dependent on the quality of the underlying approximation to CCSDT: on the asymmetric stretch  $\omega_3$ , this varies from  $+43 \text{ cm}^{-1}$  for CCSD(TQ<sub>f</sub>) via  $-6 \text{ cm}^{-1}$  for CCSDT-3(Q<sub>f</sub>) to  $-16 \text{ cm}^{-1}$  for CCSDT(Q<sub>f</sub>).

Pabst et al. [31] found that the popular CC2 approximation [32–34] to CCSD predicts a barrier-less dissociation of ozone to separate atoms – a plain chemical absurdity, which illustrates the challenging character of this system from an electronic structure point of view.

Karton and Martin in their 2010 paper [17] carried out pointwise W4 calculations and found harmonic frequencies  $\omega_1 = 1133.9$ ,  $\omega_2 = 715.2$ , and  $\omega_3 = 1067.1 \text{ cm}^{-1}$ , compared to values extracted from experiment [35] (see also Ref. [36]) of  $1133.3(4)$ ,  $715.0(4)$ , and  $1087.3(3) \text{ cm}^{-1}$ , respectively. Upon truncating the W4 model at CCSDT and CCSDTQ levels and comparing the two, it appeared that connected quadruples affect the stretching frequencies by about  $15 \text{ cm}^{-1}$ .

In terms of multireference calculations, Peterson and coworkers [37] were able to achieve agreement to  $13 \text{ cm}^{-1}$  with CAS(12,9)-icMRCI+Q/cc-pVQZ, where CAS(12,9) refers to CASSCF [38] with an active space of 12 electrons in 9 orbitals (i.e. full valence minus the 2s orbitals on each oxygen), icMRCI stands for internally contracted multireference configuration interaction [39,40], and Q refers to adding the multireference analog [41] of the Davidson correction [42]. This remaining error was removed in a subsequent study by

Szalay and coworkers [43,44] where the active space was enlarged to CAS(18,12) full valence. While this may seem to be the answer to a quantum chemist's prayer, full-valence CAS-icMRCI is no longer a feasible approach for molecules with more than four nonhydrogen atoms, owing to the factorial cost scaling of CASSCF with the numbers of electrons and active orbitals.

Li and Paldus [45] were able to obtain an at least qualitatively correct answer using 3R-CCSD (three-reference CCSD), where the three reference determinants were [...] (HOMO)<sup>2</sup>(LUMO)<sup>0</sup>, [...] (HOMO)<sup>0</sup>(LUMO)<sup>2</sup>, and [...] (HOMO)<sup>1</sup>(LUMO)<sup>1</sup>; if they omitted the third reference, poor results were obtained. In a related vein, Szalay and Bartlett [46] found in the original paper defining the AQCC (averaged quadratic coupled cluster) method that 2R-CI (two-reference CI) and 2R-ACPF (averaged coupled pair functional [47]) failed, but 2R-AQCC held its own. Hanauer and Köhn, in their paper [48] on internally contracted multireference coupled cluster, found that CAS(2,2)-icCCSDT with adequately large basis sets yielded good agreement with experiment.

## 2. Computational methods

The diatomic molecule electronic structure calculations were carried out using the arbitrary-order coupled cluster implementation [14,49–51] in the MRCC program system of Kállay and coworkers [52].

Total energies were converged to 10<sup>-11</sup> hartree or better; coupled cluster jobs were run in 'sequential restart' fashion where, e.g. CCSDT takes initial  $T_1$  and  $T_2$  amplitudes from the converged CCSD calculation, CCSDTQ in turn uses the converged CCSDT amplitudes as initial guesses for the  $T_1$ ,  $T_2$ , and  $T_3$  amplitudes, and so forth. For the open-shell species, unrestricted Hartree-Fock references were used throughout except where explicitly stated otherwise.

Basis sets used were the Dunning correlation consistent [53] cc-pVDZ, cc-pVTZ, and cc-pVQZ family.

Total energies for each diatomic were evaluated at 21 points at a spacing of 0.01 Å, ten points each forward and backward around the experimental bond distance rounded to 2 decimal places. The latter was taken from Huber and Herzberg [54].

Potential curves were then fitted, and a Dunham analysis [55] carried out, using the program `dunham` written by one of us (JMLM) in his graduate student days. First the lowest energy point  $r_i$  among the input points was found; then polynomials of increasing order in  $r - r_i$  were fitted, and the goodness of fit subjected to a standard F-test. The highest order polynomial for which the addition of an extra term was still  $\geq 99.9\%$  statistically significant was retained (in practice, this was order 7–9

for the molecules considered here). Then the minimum  $r_e$  of this polynomial was found by the Newton-Raphson approach, the polynomial re-expanded in the dimensionless Dunham variable  $(r - r_e)/r_e$ , and finally the Dunham analysis proper carried out, including propagation of the fit uncertainties.

The diatomic molecules included were a mix of:

- closed-shell 1st-row: C<sub>2</sub>, CO, N<sub>2</sub>, BN, BF, F<sub>2</sub>, BH, CH, NH, OH, HF;
- closed-shell heavy atom 2nd-row and mixed: PN, P<sub>2</sub>, SiO, CS, HCl;
- open-shell: B<sub>2</sub>, O<sub>2</sub>, S<sub>2</sub>, SO, CN.

These molecules span a broad range of nondynamical correlation character, from dominated by dynamical correlation (such as HF and BF) to pathologically strong static correlation in C<sub>2</sub> and BN, and all gradations in between. This is illustrated by the vector norms and maximum elements of the  $T_1$ ,  $T_2$ ,  $T_3$ , and  $T_4$  vectors of the molecules (Table 1). The  $T_1$  diagnostic of Lee and Taylor [56] (see also Ref. [57]) is given as well as the  $D_1$  diagnostic [58] of Nielsen and Janssen and the  $D_2$  diagnostic of the same authors [59]. By extension from Ref. [56] we also obtained

$$\mathcal{T}_n = ||T_n||/N_e^{1/2} \quad (1)$$

where  $T_n$  is the cluster amplitudes vector for  $n$ -tuple substitutions and  $N_e$  represents the number of (in this case, valence) electrons being correlated. For closed-shell cases and  $n = 1$ , Equation (1) is equivalent to the original  $T_1$  diagnostic if core electrons are excluded.

The non- $\Lambda$  levels of coupled cluster theory considered include CCSD [3], CCSD[T] (a.k.a., CCSD+T(CCSD)), [60] CCSD(T), [1,2] CCSDT, [60] CCSDT[Q], [61] CCSDT(Q), [14] CCSDT(Q)<sub>A</sub>, [50] CCSDT(Q)<sub>B</sub>, [50] CCSDTQ, [62] CCSDTQ(5), [50] and CCSDTQ5 [63].

Lambda approaches were introduced independently from different considerations by Stanton et al. [20,21] and by Kucharski and Bartlett [22,23].

In order to be able to consider the broadest variety of approximate methods, UHF references were used throughout. Initially we had included the NO molecule in our sample as well: however, it quickly became apparent that its calculated potential curves were too noisy to allow for Dunham fits of acceptably high order. This is a consequence of the UHF solution for this molecule bifurcating [64] near the equilibrium bond distance. The corresponding ROHF-reference potential curves were devoid of similar noise and could be fitted to 8<sup>th</sup> order without problems. As this, however, would mean skipping NO for part of the data columns where no ROHF

**Table 1.** Diagnostics at the CCSDTQ/cc-pVDZ level.

	$T_1$	$T_2$	$T_3$	$T_4$	$\max T_1$	$\max T_2$	$\max T_3$	$\max T_4$	$D_1$	$D_2$
CN	<b>0.099</b>	0.100	<b>0.020</b>	0.005	<b>0.263</b>	0.119	0.018	0.003	<b>0.154</b>	0.195
Cl <sub>2</sub>	0.007	0.070	0.009	0.001	0.017	0.121	0.003	0.000	0.021	0.184
BF	0.016	0.075	0.010	0.002	0.030	0.119	0.006	0.002	0.037	0.228
SO	0.016	0.073	0.012	0.002	0.035	0.110	0.012	0.001	0.044	0.156
C <sub>2</sub>	0.037	<b>0.154</b>	<b>0.030</b>	<b>0.008</b>	0.085	<b>0.399</b>	0.019	0.006	0.087	<b>0.385</b>
CO	0.017	0.077	0.014	0.003	0.030	0.086	0.013	0.004	0.044	0.160
CS	0.024	0.093	0.019	0.005	0.037	0.115	0.016	0.005	0.056	0.183
BH	0.013	0.109	0.011	0.002	0.016	0.122	0.005	0.001	0.026	0.266
S <sub>2</sub>	0.014	0.081	0.014	0.003	0.033	0.120	0.007	0.002	0.017	0.158
CH	0.010	0.083	0.009	0.001	0.012	0.108	0.006	0.001	0.016	0.203
PN	0.018	0.098	0.019	0.005	0.021	0.148	0.010	0.003	0.037	0.211
O <sub>2</sub>	0.013	0.068	0.009	0.002	0.033	0.123	0.005	0.003	0.013	0.133
OH	0.005	0.056	0.004	0.001	0.007	0.053	0.002	0.000	0.012	0.129
P <sub>2</sub>	0.016	0.105	0.021	0.005	0.030	0.155	0.009	0.004	0.033	0.218
HF	0.004	0.051	0.003	0.001	0.006	0.053	0.002	0.000	0.014	0.115
B <sub>2</sub>	0.036	<b>0.154</b>	<b>0.037</b>	<b>0.010</b>	0.072	<b>0.355</b>	<b>0.027</b>	<b>0.016</b>	0.073	<b>0.395</b>
N <sub>2</sub>	0.011	0.080	0.012	0.003	0.018	0.113	0.006	0.004	0.026	0.176
BN	<b>0.082</b>	<b>0.143</b>	<b>0.039</b>	<b>0.012</b>	<b>0.215</b>	<b>0.346</b>	<b>0.046</b>	<b>0.012</b>	<b>0.196</b>	<b>0.328</b>
F <sub>2</sub>	0.009	0.065	0.008	0.001	0.022	0.209	0.004	0.001	0.032	0.245
NO	0.030	0.074	0.013	0.002	0.094	0.138	0.022	0.001	0.054	0.186
NH	0.008	0.061	0.005	0.001	0.014	0.048	0.002	0.000	0.010	0.142
SiO	0.029	0.088	<b>0.020</b>	0.006	0.058	0.088	0.022	<b>0.011</b>	0.066	0.195
O <sub>3</sub>	0.030	0.089	<b>0.020</b>	0.005	0.086	<b>0.314</b>	<b>0.023</b>	0.002	0.078	0.278

Reference geometries were CCSDTQ5(6)<sub>Λ</sub>/cc-pVDZ. Conspicuously large values in a given column are bolded.

implementation is available, we deleted NO from the analysis.

Single-reference equilibrium geometries and harmonic vibrational frequencies of ozone were determined using the CFOUR program package [65]. The correlation consistent cc-pVDZ basis set of Dunning and coworkers [53] was used with a restricted Hartree-Fock (RHF) reference for calculations ranging from CCSD [3] to CCSDTQ5 [63]. Aside from approximate coupled cluster approaches such as asymmetric (lambda-based) methods like CCSD(T)<sub>Λ</sub>, more familiar symmetric counterparts (like CCSD(T) [1,2] and its precursor CCSD+T(CCSD), [60] a.k.a. CCSD[T]) were included in this study. Calculations requiring up to full quadruple excitations, CCSDTQ [62], were carried out with the NCC program developed by Matthews and coworkers [65], while those incorporating higher excitations used MRCC [52].

Total energies were converged to at least the ninth decimal place for CCSDTQ(5), CCSDTQ(5)<sub>Λ</sub>, and CCSDTQ5, and beyond the tenth decimal place for all lower levels. For levels of theory possessing implemented analytic gradients (up to CCSDTQ, excluding CCSDT[Q] [61] and CCSDT(Q)<sub>Λ</sub>), ozone harmonic force fields were calculated via numerical differentiation of analytically evaluated forces. Otherwise, harmonic frequencies were determined through double numerical differentiation of energies. Comparisons between harmonic force fields evaluated at the CCSD(T) level indicated that these partially numerical methods yield frequencies within 0.1 cm<sup>-1</sup> of the ‘exact’ values obtained through analytical second derivatives [66,67] of CCSD(T).

Multireference calculations were performed using MOLPRO 2022.3 [68], which was also employed for the large basis CCSD(T) steps in some of the composite schemes discussed below.

## 3. Results and discussion

### 3.1. Diatomics

For the small cc-pVDZ basis set, we can easily go all the way up to connected sextuple excitations. Table 2 presents the performance statistics in the cc-pVDZ basis set of the various coupled cluster approximations for the following four quantities: bond distance  $r_e$ , harmonic frequency  $\omega_e$ , first anharmonicity constant  $\omega_e x_e$ , and rotation-vibration coupling constant  $\alpha_e$ . (Note that these quantities require at most fourth derivatives, for  $\omega_e x_e$ , and that we have enough data points that we can reliably fit sixth- or higher-order expansions.)

First of all, the difference between CCSDTQ5(6)<sub>Λ</sub> and fully iterative CCSDTQ56 is negligible, at 0.002 kcal/mol RMSD. Only for one diatomic, C<sub>2</sub>, does it reach 0.01 kcal/mol. We thus deem it justified to use CCSDTQ5(6)<sub>Λ</sub> as our quasi-full CI reference. The complete sextuples contribution CCSDTQ56 – CCSDTQ5 works out to 0.018 kcal/mol RMS and –0.009 kcal/mol MSD. The large RMSD/MAD ratio indicates an outlier (for an unbiased normal distribution, RMSD/MAD =  $\sqrt{\pi/2} \approx 5/4$  [18,69]), which turns out to be C<sub>2</sub> at 0.068 kcal/mol.

Second, it is immediately apparent from the spectroscopic constants that the effect of sextuples is negligible



**Table 2.** Root mean square deviations (RMSD), mean signed deviations (MSD), and mean absolute deviations (MAD) for diatomic spectroscopic constants from the CCSDTQ5(6)<sub>Λ</sub> level with the cc-pVDZ basis set.

	$r_e$ (Å)		$\omega_e$ (cm <sup>-1</sup> )		$\omega_e x_e$ (cm <sup>-1</sup> )		$\alpha_e$ (cm <sup>-1</sup> )		$D_e$ (kcal/mol)		
	RMSD	MSD	RMSD	MSD	RMSD	MSD	RMSD	MSD	RMSD	MSD	MAD
CCSD	0.01215	-0.00975	59.6	49.7	1.34	-1.08	0.00494	-0.00268	7.763	-6.193	6.193
CCSD[T]	0.00814	-0.00213	36.3	8.1	5.33	1.08	0.00162	-0.00011	1.704	0.235	0.811
CCSD(T)	0.00395	-0.00281	20.2	14.2	1.89	0.09	0.00147	-0.00059	0.955	-0.719	0.741
CCSD(T) <sub>Λ</sub>	0.00395	-0.00287	32.4	19.2	0.57	0.30	0.00171	-0.00078	1.289	-0.960	0.960
CCSDT	0.00240	-0.00184	14.3	10.4	0.42	-0.20	0.00046	-0.00028	0.931	-0.737	0.737
CCSDT[Q]	0.00222	-0.00045	10.1	4.5	0.53	-0.22	0.00031	-0.00016	0.670	-0.386	0.388
CCSDT(Q)	0.00078	-0.00003	6.5	-1.7	0.45	0.12	0.00040	0.00007	0.248	0.104	0.125
ditto w/o BN	0.00039	0.00012	3.4	-0.5	0.16	0.03	0.00014	0.00000	0.181	0.071	0.092
CCSDT(Q) <sub>A</sub>	0.00160	-0.00004	7.4	1.7	0.53	-0.20	0.00019	-0.00008	0.366	-0.104	0.156
CCSDT(Q) <sub>B</sub>	0.00101	0.00005	8.0	0.0	0.55	-0.17	0.00027	-0.00010	0.199	-0.029	0.098
ditto w/o BN	0.00044	-0.00015	4.0	1.5	0.24	-0.07	0.00018	-0.00006	0.127	0.004	0.068
CCSDT(Q) <sub>Λ</sub>	0.00031	-0.00008	3.0	0.4	0.22	-0.07	0.00017	-0.00005	0.106	0.004	0.057
ditto w/o BN	0.00027	-0.00012	2.2	0.9	0.22	-0.08	0.00015	-0.00007	0.100	-0.005	0.051
CCSDTQ	0.00041	-0.00026	2.5	1.5	0.11	-0.02	0.00007	-0.00002	0.128	-0.080	0.083
ditto w/o BN	0.00039	-0.00024	2.5	1.4	0.08	-0.04	0.00006	-0.00003	0.124	-0.075	0.078
CCSDTQ[5]	0.00037	-0.00004	2.3	0.7	0.13	-0.05	0.00006	-0.00002	0.075	-0.026	0.035
CCSDTQ(5)	0.00037	-0.00004	2.3	0.7	0.13	-0.05	0.00006	-0.00002	0.075	-0.026	0.035
CCSDTQ(5) <sub>A</sub>	0.00032	-0.00007	2.0	0.9	0.12	-0.05	0.00006	-0.00003	0.075	-0.033	0.036
CCSDTQ(5) <sub>B</sub>	0.00037	-0.00005	2.2	0.7	0.14	-0.06	0.00006	-0.00003	0.082	-0.032	0.037
CCSDTQ(5) <sub>Λ</sub>	0.00007	-0.00003	0.5	0.2	0.02	-0.01	0.00002	-0.00001	0.016	-0.006	0.011
CCSDTQ5	0.00005	-0.00003	0.3	0.2	0.01	0.00	0.00001	0.00000	0.018	-0.009	0.010
CCSDTQ5[6]	0.00003	-0.00002	0.2	0.1	0.01	0.00	0.00000	0.00000	0.014	-0.007	0.008
CCSDTQ5(6)	0.00005	-0.00001	0.4	0.1	0.03	-0.01	0.00001	0.00000	0.006	-0.002	0.003
CCSDTQ5(6) <sub>A</sub>	0.00004	-0.00001	0.3	0.1	0.02	-0.01	0.00001	0.00000	0.007	-0.003	0.003
CCSDTQ5(6) <sub>B</sub>	0.00004	-0.00001	0.4	0.1	0.03	-0.01	0.00001	0.00000	0.007	-0.003	0.003
CCSDTQ5(6) <sub>Λ</sub>	REF	REF	REF	REF	REF	REF	REF	REF	0.002	0.000	0.001
CCSDTQ56	-	-	-	-	-	-	-	-	REF	REF	REF

for all but the most demanding applications – 0.00005 Å for  $r_e$ , 0.3 cm<sup>-1</sup> for harmonic frequencies, 0.01 cm<sup>-1</sup> for the anharmonic constant, and 0.00001 cm<sup>-1</sup> for the rovibrational coupling constant.

Third, the difference between CCSDTQ(5)<sub>Λ</sub> and fully iterative CCSDTQ5 is similarly small – and the two tiny differences even partially compensate, as reflected in the CCSDTQ5(6)<sub>Λ</sub> – CCSDTQ(5)<sub>Λ</sub> difference. In light of the fact that CCSDTQ(5)<sub>Λ</sub> is vastly cheaper than fully iterative CCSDTQ5 – asymptotically scaling as  $O(n^5 N^6)$  rather than  $O(n^5 N^7)$  – this would seem to be a good choice for a reference level. The superiority of CCSDTQ(5)<sub>Λ</sub> over CCSDTQ(5) was previously noted for the 8-valence electron diatomics [72].

Fourth, the apparent effect of connected quintuple excitations is to lengthen bonds by an average of 0.0002 Å, concomitantly with an average decrease in the harmonic frequency by 1.3 cm<sup>-1</sup> and a negligible average increase in the anharmonicity of just 0.02 cm<sup>-1</sup>. However, for some molecules like N<sub>2</sub> and PN, the difference may reach a less trivial 4–5 cm<sup>-1</sup>.

Fifth, the other approximate quintuples treatments such as CCSDTQ(5) are all clearly inferior in quality to CCSDTQ(5)<sub>Λ</sub>, and it is not even clear that they are superior to CCSDTQ.

Sixth, the performance difference between CCSDTQ and CCSDT(Q)<sub>Λ</sub> is remarkably small, and much of that

difference can in fact be attributed to the pathologically multireference BN diatomic – which is a taxing test for any electron correlation method, and *a fortiori* for any quasiperturbative correction. Except for the cases of CN and BN, it is not obvious that CCSDT(Q)<sub>Λ</sub> agrees less well with the reference than does CCSDTQ: indeed, upon removal of BN, statistics for harmonic frequencies at the CCSDT(Q)<sub>Λ</sub> level are superior to those of CCSDTQ. Again, the reduced scaling by  $O(n^4 N^5)$  instead of  $O(n^4 N^6)$  is a great boon.

Seventh, CCSDT(Q)<sub>Λ</sub> is clearly superior to CCSDT(Q). CCSDT(Q)<sub>B</sub> represents no obvious improvement over CCSDT(Q). Superior performance of CCSDT(Q)<sub>Λ</sub> over other quasiperturbative quadruples options was first noted for a smaller sample of eight-valence-electron species in Ref. [72].

For further comparison, let us turn to the cc-pVTZ basis set (Table 3). The observations above are largely seen here as well. CCSDT(Q)<sub>Λ</sub> is again found to be a felicitous compromise between performance and computational cost: the shortcomings of the other approximate connected quadruples methods are actually clearest in the anharmonicity constant, and to a lesser extent in the rovibrational coupling constant and the bond distance. The large RMSD/MSD ratio for the  $D_e$  contribution indicates an outlier, which is B<sub>2</sub> at 0.36 kcal/mol. Note from Table 1 that B<sub>2</sub> has an unusually large  $T_4$  amplitude of

**Table 3.** Root mean square deviations (RMSD), mean signed deviations (MSD), and mean absolute deviations (MAD) for diatomic spectroscopic constants from the CCSDTQ(5)<sub>Λ</sub> level with the cc-pVTZ basis set.

	$r_e$ (Å)		$\omega_e$ (cm <sup>-1</sup> )		$\omega_e x_e$ (cm <sup>-1</sup> )		$\alpha_e$ (cm <sup>-1</sup> )		$D_e$ (kcal/mol))		
	RMSD	MSD	RMSD	MSD	RMSD	MSD	RMSD	MSD	RMSD	MSD	MAD
CCSD	0.0114	-0.0093	60.0	50.3	1.26	-0.93	0.00487	-0.00273	8.814	-7.220	7.220
CCSD[T]	0.0068	-0.0019	32.6	8.1	4.21	0.74	0.00122	-0.00020	1.597	0.442	0.644
<b>CCSD(T)</b>	0.0034	-0.0024	20.1	13.4	1.37	-0.01	0.00131	-0.00066	0.714	-0.460	0.494
CCSD(T) <sub>Λ</sub>	0.0035	-0.0026	31.0	18.8	1.52	0.00	0.00170	-0.00099	1.189	-0.842	0.842
CCSDT	0.0024	-0.0018	14.0	10.5	0.41	-0.21	0.00057	-0.00034	1.071	-0.829	0.829
CCSDT[Q]	0.0020	-0.0006	9.3	4.6	0.47	-0.21	0.00029	-0.00020	0.881	-0.598	0.599
CCSDT(Q)	0.0009	0.0000	5.2	-1.9	0.53	0.13	0.00039	0.00008	0.265	0.111	0.124
ditto w/o BN	0.0003	0.0001	2.0	-0.9	0.14	0.02	0.00012	0.00001	0.187	0.075	0.088
CCSDT(Q) <sub>A</sub>	0.0014	0.0000	5.9	1.2	0.37	-0.14	0.00013	-0.00006	0.368	-0.118	0.158
CCSDT(Q) <sub>B</sub>	0.0008	0.0000	7.6	-0.6	0.50	-0.15	0.00021	-0.00008	0.203	-0.039	0.096
ditto w/o BN	0.0003	-0.0001	2.8	0.9	0.21	-0.06	0.00015	-0.00005	0.123	-0.006	0.065
<b>CCSDT(Q)<sub>Λ</sub></b>	0.0002	-0.0001	2.4	0.3	0.19	-0.07	0.00015	-0.00004	0.090	-0.006	0.045
ditto w/o BN	0.0002	-0.0001	1.4	0.7	0.19	-0.07	0.00013	-0.00006	0.091	-0.010	0.044
CCSDTQ	0.0004	-0.0002	2.1	1.4	0.08	-0.02	0.00006	-0.00002	0.122	-0.081	0.082
CCSDTQ[5]	0.0004	0.0000	2.1	0.5	0.12	-0.03	0.00005	-0.00002	0.100	-0.044	0.049
CCSDTQ(5)	0.0004	0.0000	2.1	0.5	0.12	-0.03	0.00005	-0.00002	0.100	-0.044	0.049
CCSDTQ(5) <sub>A</sub>	0.0003	0.0000	1.9	0.6	0.11	-0.04	0.00005	-0.00002	0.102	-0.050	0.050
CCSDTQ(5) <sub>B</sub>	0.0004	0.0000	2.0	0.5	0.13	-0.04	0.00005	-0.00002	0.109	-0.049	0.052
CCSDTQ(5) <sub>Λ</sub>	REF	REF	REF	REF	REF	REF	REF	REF	REF	REF	REF

0.016, with only the pathologically multireference BN molecule even coming close at 0.012.

In terms of contributions to the dissociation energy, predictably there are differences between the basis sets for CCSD, CCSD(T), and to a lesser extent CCSDT. However, from CCSDT(Q) onward, the differences with the reference are remarkably similar between the cc-pVDZ and cc-pVTZ basis sets, which reflects the observation from Refs. [4,5] that basis set convergence of terms in the cluster expansion becomes ever faster as one walks up the substitution ladder.

Comparison between CCSDT and CCSDTQ reveals that connected quadruples lengthen bonds across the board, by an average of 0.0016 Å, and reduce harmonic frequencies by an average of 8.9 cm<sup>-1</sup>. With the exception of BN, anharmonicities are slightly increased as well (0.18 cm<sup>-1</sup> on average) by connected quadruples.

Full CCSDT minus CCSD(T) is more of a mixed bag, with bond contractions seen in P<sub>2</sub>, PN, N<sub>2</sub>, and O<sub>2</sub>, and lengthening in the other diatomics (translating into an average lengthening by 0.0018 Å). Significantly, the error statistics for harmonic frequencies are not that dissimilar between CCSDT and CCSD(T): it is in the anharmonicity and rovibrational coupling constants that CCSDT is clearly superior. The other approximate triples contributions are inferior to CCSD(T) in performance.

The RMSD of 14 cm<sup>-1</sup> for CCSD(T) seems to be at odds with the 5 cm<sup>-1</sup> reported in Ref. [16] for HFREQ27. However, said set was long on species such as C<sub>2</sub>H<sub>4</sub>, N<sub>2</sub>H<sub>4</sub>, CH<sub>3</sub>OH, and the like, where the X-H stretching frequencies are much easier to describe without high-order connected excitations.

Is there a need to consider larger basis sets? Comparing Tables 2 and 3, we note that the difference in statistics becomes quite small for CCSDT and insignificant for higher levels. This would seem to make proceeding further to cc-pVQZ redundant; nevertheless, by way of verification, we did carry out CCSDTQ(5)<sub>Λ</sub>/cc-pVQZ calculations for B<sub>2</sub>, C<sub>2</sub>, N<sub>2</sub>, and P<sub>2</sub>. The differences from CCSDTQ(5)<sub>Λ</sub> for those four molecules are compared between cc-pVTZ and cc-pVQZ in Table 4. Their trends clearly parallel what has been reported above – most saliently, that agreement of CCSDT(Q)<sub>Λ</sub> with CCSDTQ(5)<sub>Λ</sub> meets or exceeds that of fully iterative CCSDTQ.

### 3.2. Composite schemes and comparison with experiment

Some might argue that thus far, we have been comparing to putative full CI limits for finite basis sets, and that we ought to consider comparison with experiment instead. For all diatomics considered here except BN, reliable experimental spectroscopic constants are available from Irikura [70] or from the older, but still widely used, Huber and Herzberg reference book [54]. To this end, we obtained potential curves using a simple composite scheme in which all-electron CCSD(T) including X2C (exact two-component [71]) corrections was supplemented with an additive post-CCSD(T) correction of the form, e.g. E[CCSD(T)/LARGE+CV+REL]+E[CCSDT(Q)/SMALL] – E[CCSD(T)/SMALL]. The resulting error statistics can be found in Table 5.

**Table 4.** Comparison for selected diatomics between cc-pVQZ and cc-pVTZ basis sets for differences ( $\text{\AA}, \text{cm}^{-1}$ ) with CCSDTQ(5) $_{\Lambda}$ .

B <sub>2</sub>	cc-pVQZ				cc-pVTZ			
	$\Delta R_e$	$\Delta \omega_e$	$\Delta \omega_e X_e$	$\Delta \alpha_e$	$\Delta R_e$	$\Delta \omega_e$	$\Delta \omega_e X_e$	$\Delta \alpha_e$
CCSD(T)	-0.00408	8.20	-0.004	0.00002	-0.00424	8.49	-0.016	0.00001
CCSD(T) $_{\Lambda}$	-0.00196	5.76	-0.010	-0.00001	-0.00221	5.95	-0.022	-0.00002
CCSDT	-0.00059	-0.52	0.050	0.00010	-0.00061	-0.42	0.041	0.00009
CCSDT(Q)	-0.00036	-0.01	0.021	0.00004	-0.00032	-0.05	0.018	0.00004
CCSDT(Q)/B	-0.00067	0.95	0.034	0.00003	-0.00062	0.87	0.032	0.00003
CCSDT(Q) $_{\Lambda}$	-0.00043	0.48	0.024	0.00003	-0.00043	0.47	0.021	0.00003
CCSDTQ	-0.00002	-0.31	0.012	0.00002	-0.00001	-0.33	0.010	0.00002
CCSDTQ(5)	-0.00013	0.47	-0.003	-0.00001	-0.00012	0.45	-0.003	-0.00001
CCSDTQ(5) <sub>B</sub>	-0.00013	0.44	-0.001	-0.00001	-0.00012	0.42	-0.002	-0.00001
C <sub>2</sub>	$\Delta R_e$	$\Delta \omega_e$	$\Delta \omega_e X_e$	$\Delta \alpha_e$	$\Delta R_e$	$\Delta \omega_e$	$\Delta \omega_e X_e$	$\Delta \alpha_e$
CCSD(T)	-0.00195	15.44	-1.030	-0.00061	-0.00204	15.63	-0.996	-0.00059
CCSD(T) $_{\Lambda}$	-0.00077	17.77	-1.299	-0.00085	-0.00092	18.12	-1.271	-0.00084
CCSDT	-0.00218	17.53	-0.886	-0.00058	-0.00217	17.50	-0.870	-0.00057
CCSDT(Q)	0.00031	-1.67	-0.098	-0.00004	0.00032	-1.55	-0.100	-0.00004
CCSDT(Q)/B	-0.00016	1.93	-0.086	-0.00007	-0.00015	2.02	-0.083	-0.00008
CCSDT(Q) $_{\Lambda}$	0.00006	2.65	-0.482	-0.00028	0.00006	2.75	-0.479	-0.00028
CCSDTQ	-0.00049	2.99	-0.052	-0.00004	-0.00048	2.93	-0.046	-0.00004
CCSDTQ(5)	0.00010	-0.60	0.051	0.00002	0.00010	-0.63	0.052	0.00002
CCSDTQ(5) <sub>B</sub>	0.00005	-0.27	0.051	0.00002	0.00005	-0.30	0.051	0.00002
N <sub>2</sub>	$\Delta R_e$	$\Delta \omega_e$	$\Delta \omega_e X_e$	$\Delta \alpha_e$	$\Delta R_e$	$\Delta \omega_e$	$\Delta \omega_e X_e$	$\Delta \alpha_e$
CCSD(T)	-0.00095	12.58	-0.319	-0.00024	-0.00098	12.89	-0.335	-0.00025
CCSD(T) $_{\Lambda}$	-0.00124	15.86	-0.374	-0.00029	-0.00125	15.94	-0.391	-0.00030
CCSDT	-0.00163	22.50	-0.577	-0.00045	-0.00162	22.55	-0.593	-0.00046
CCSDT(Q)	0.00015	-2.73	0.157	0.00009	0.00014	-2.65	0.160	0.00009
CCSDT(Q)/B	0.00010	-2.00	0.140	0.00008	0.00009	-1.96	0.146	0.00008
CCSDT(Q) $_{\Lambda}$	0.00005	-0.98	0.070	0.00004	0.00004	-0.88	0.070	0.00004
CCSDTQ	-0.00024	3.82	-0.141	-0.00010	-0.00024	3.75	-0.142	-0.00010
CCSDTQ(5)	0.00002	-0.66	0.060	0.00003	0.00002	-0.68	0.061	0.00003
CCSDTQ(5) <sub>B</sub>	0.00001	-0.47	0.049	0.00003	0.00002	-0.49	0.049	0.00003
P <sub>2</sub>	$\Delta R_e$	$\Delta \omega_e$	$\Delta \omega_e X_e$	$\Delta \alpha_e$	$\Delta R_e$	$\Delta \omega_e$	$\Delta \omega_e X_e$	$\Delta \alpha_e$
CCSD(T)	-0.00324	9.40	-0.160	-0.00005	-0.00360	10.45	-0.186	-0.00006
CCSD(T) $_{\Lambda}$	-0.00527	14.60	-0.213	-0.00007	-0.00562	15.58	-0.241	-0.00008
CCSDT	-0.00512	14.85	-0.188	-0.00007	-0.00528	15.25	-0.194	-0.00007
CCSDT(Q)	0.00023	-1.22	0.060	0.00001	0.00021	-1.18	0.069	0.00001
CCSDT(Q)/B	0.00005	-0.73	0.057	0.00001	0.00003	-0.73	0.066	0.00001
CCSDT(Q) $_{\Lambda}$	-0.00040	1.01	0.006	0.00000	-0.00045	1.10	0.010	0.00000
CCSDTQ	-0.00084	2.76	-0.045	-0.00002	-0.00086	2.77	-0.044	-0.00002
CCSDTQ(5)	-0.00005	-0.23	0.024	0.00001	-0.00002	-0.32	0.025	0.00001
CCSDTQ(5) <sub>B</sub>	-0.00008	-0.11	0.020	0.00000	-0.00005	-0.19	0.021	0.00000
BN	$\Delta R_e$	$\Delta \omega_e$	$\Delta \omega_e X_e$	$\Delta \alpha_e$	$\Delta R_e$	$\Delta \omega_e$	$\Delta \omega_e X_e$	$\Delta \alpha_e$
CCSD(T)	-0.01004	44.54	5.456	0.00081	-0.01110	42.10	6.313	0.00130
CCSD(T) $_{\Lambda}$	-0.00376	77.56	4.088	-0.00127	-0.00486	82.44	6.511	-0.00073
CCSDT	-0.00263	7.77	0.991	0.00059	-0.00256	6.91	0.937	0.00060
CCSDT(Q)	-0.00443	-20.58	2.561	0.00175	-0.00409	-23.25	2.444	0.00178
CCSDT(Q)/B	0.00323	-35.31	-2.098	-0.00056	0.00352	-33.99	-2.167	-0.00071
CCSDT(Q) $_{\Lambda}$	0.00069	-8.98	0.071	0.00034	0.00074	-9.39	-0.007	0.00033
CCSDTQ	-0.00078	2.51	0.294	0.00017	-0.00076	2.27	0.275	0.00017
CCSDTQ(5)	0.00132	-1.02	-0.181	-0.00008	0.00126	-0.83	-0.173	-0.00009
CCSDTQ(5) <sub>B</sub>	0.00134	-2.51	-0.368	-0.00010	0.00129	-2.22	-0.370	-0.00012

Due to resource constraints, post-CCSDTQ for BN was obtained by the pointwise additivity approximation  $E[\text{CCSDTQ}(5)_{\Lambda}/\text{cc-pVQZ}] \approx E[\text{CCSDTQ}/\text{cc-pVQZ}] + E[\text{CCSDTQ}(5)_{\Lambda}/\text{cc-pVQZ}(\text{no g})] - E[\text{CCSDTQ}/\text{cc-pVQZ}(\text{no g})]$

We use here the X2C reconstructions, provided in the MOLPRO basis set library, of the aug-cc-pCV5Z basis set [73] combined with aug-cc-pV5Z [74] on hydrogen.

Without post-CCSD(T) corrections, bond distances are systematically too short (and hence, due to Badger's rule [75]) harmonic frequencies systematically blue-shifted. RMS error in  $\omega_e$  reaches nearly  $10 \text{ cm}^{-1}$ , and  $0.5 \text{ cm}^{-1}$  in the first anharmonic correction. Expanding the basis set further in fact increases these errors.

Including just a CCSDT correction somewhat reduces bond compression, but does not improve statistics overall.

A CCSDT(Q)/cc-pVTZ correction slightly overcorrects bond lengths – leading to slightly too low harmonic frequencies, but a much improved RMSD of  $3.6 \text{ cm}^{-1}$ , while that for anharmonicity constants improves to  $0.18 \text{ cm}^{-1}$ . Substituting CCSDT(Q) $_{\Lambda}$ , however, reduces the systematic underestimate of harmonic frequencies to



**Table 5.** RMSD and MSD (Root Mean Square and Mean Signed Deviations in Å,cm<sup>-1</sup>) of spectroscopic constants from experiment with various composite schemes.

CCSD(T) component	post-CCSD(T) correction	RMSD	RMSD	RMSD	MSD	MSD	MSD
		$\Delta r_e$	$\Delta \omega_e$	$\Delta \omega_e x_e$	$\Delta r_e$	$\Delta \omega_e$	$\Delta \omega_e x_e$
CCSD(T)/ACV5Z (NR, no CV)	nil	0.00306	6.73	0.422	0.00246	1.97	-0.299
CCSD(T)/ACV5Z (CV+NR)	nil	0.00136	10.40	0.378	-0.00090	8.90	-0.232
CCSD(T)-X2C/ACV5Z-X2C (CV+R)	nil	0.00131	9.09	0.380	-0.00088	7.47	-0.238
CCSD(T)-X2C/ACV6Z-X2C (CV+R)	nil	0.00163	9.63	0.517	-0.00147	9.15	-0.347
CCSD(T)-X2C/ACV5,6Z-X2C (CV+R)	nil	0.00233	11.03	0.748	-0.00219	10.71	-0.406
CCSD(T)-X2C/ACV5Z-X2C (CV+R)	CCSDT/cc-pVTZ	0.00148	12.54	0.392	-0.00091	8.95	-0.227
CCSD(T)-X2C/ACV5Z-X2C (CV+R)	CCSDT(Q)/cc-pVDZ <sup>a</sup>	0.00120	3.70	0.202	0.00091	-2.28	0.033
CCSD(T)-X2C/ACV5Z-X2C (CV+R)	CCSDT(Q) <sub>Λ</sub> /cc-pVDZ <sup>a</sup>	0.00100	2.46	0.235	0.00073	-1.00	-0.033
CCSD(T)-X2C/ACV5Z-X2C (CV+R)	CCSDT(Q)/cc-pVTZ <sup>a</sup>	0.00128	3.64	0.177	0.00093	-2.42	0.063
CCSD(T)-X2C/ACV5Z-X2C (CV+R)	CCSDT(Q) <sub>Λ</sub> /cc-pVTZ <sup>a</sup>	0.00103	2.09	0.198	0.00072	-0.87	-0.018
CCSD(T)-X2C/ACV5Z-X2C (CV+R)	CCSDT(Q) <sub>Λ</sub> /cc-pVTZ	0.00102	2.09	0.189	0.00073	-0.98	-0.013
CCSD(T)-X2C/ACV5Z-X2C (CV+R)	CCSDTQ(5) <sub>Λ</sub> /cc-pVTZ	0.00112	2.07	0.167	0.00082	-1.41	0.031
CCSD(T)/ACV5,6Z+ΔX2C/ACV5Z (CV+R) <sup>b</sup>	ditto	0.00058	1.93	0.200	-0.00043	1.04	-0.103
CCSD(T)-X2C/ACV5Z-X2C (CV+R)	CCSDT(Q) <sub>Λ</sub> /cc-pVQZ	0.00103	1.92	0.183	0.00074	-0.97	-0.018
CCSD(T)-X2C/ACV5,6Z-X2C (CV+R)	ditto	0.00077	2.75	0.384	-0.00049	1.54	-0.128
CCSD(T)/ACV5,6Z+ΔX2C/ACV5Z (CV+R) <sup>b</sup>	ditto	0.00071	2.49	0.257	-0.00054	1.78	-0.143
CCSD(T)-X2C/ACV5Z-X2C (CV+R)	CCSDT(Q) <sub>Λ</sub> /cc-pVQZ+CCSDTQ(5) <sub>Λ</sub> - CCSDT(Q) <sub>Λ</sub> /cc-pVTZ	0.00114	1.94	0.127	0.00083	-1.41	0.011
CCSD(T)-X2C/ACV5,6Z-X2C (CV+R)	ditto	0.00061	2.16	0.422	-0.00041	0.88	-0.063
CCSD(T)/ACV5,6Z+ΔX2C/ACV5Z (CV+R) <sup>b</sup>	ditto	0.00056	1.92	0.275	-0.00045	1.08	-0.075

NR: Non-Relativistic, R: Relativistic, CV: core-valence correlation

post-CCSD(T) corrections: CCSDT/BASIS refers to E[CCSDT/BASIS] - E[CCSD(T)/BASIS]

All expt. reference data from the compilation of Irikura [70], except B<sub>2</sub>, where they are taken from Ref. [54]

(a) Excluding CN, NO, and SO, as UHF-CCSDT(Q) unsuitable for these species and ROHF-CCSDT(Q) not implemented

(b) The ΔX2C/ACV5Z term indicates an additive relativistic correction [CCSD(T)-X2C/ACV5Z-X2C (CV+R) - CCSD(T)/ACV5Z (CV)], where X2C is the 'exact two-component' approach [71].

less than 1 cm<sup>-1</sup>, and hence RMSD further to 2.1 cm<sup>-1</sup>. This appears to be the 'Pareto optimum' for this simple combination: upgrading the post-CCSD(T) correction further to CCSDTQ(5)<sub>Λ</sub> does not result in any significant further improvement in the harmonic frequencies, though the RMSD in the anharmonicity constants is reduced slightly further, for 0.19 to 0.17 cm<sup>-1</sup>. These 'diminishing returns' do not justify the massive cost increase.

Increasing the underlying basis set for CCSD(T) to 6Z causes major near-linear dependence issues for some molecules when X2C is enabled; for the remainder, it appears that with the CCSDTQ(5)<sub>Λ</sub> correction, RMSD for bond distances can be reduced to 0.0006 Å (mean signed error -0.0004 Å).

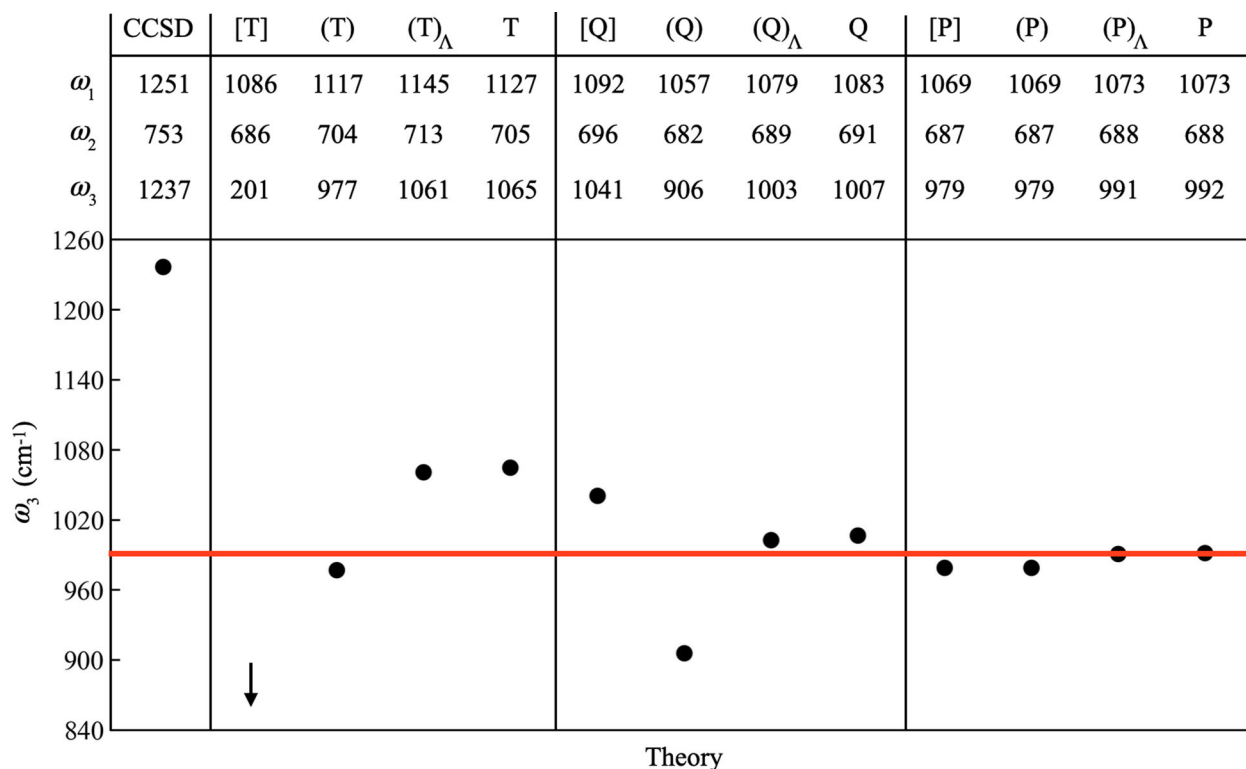
We attempted both increasing the basis set for (Q)<sub>Λ</sub> to cc-pVQZ and additionally including a CCSDTQ(5)<sub>Λ</sub>-CCSDT(Q)<sub>Λ</sub> correction with the cc-pVTZ basis set. Neither is able to do substantially better than 2 cm<sup>-1</sup> for harmonic frequencies - which appears to be the practical limit in this 'CCSD(T) plus corrections' framework. Additionally improving the CCSD(T) part by considering a ACV5,6Z basis set extrapolation does not improve the frequencies much, although bond lengths are now substantially better than 0.001 Å RMS.

This relative insensitivity to the quality of the basis set in the post-CCSD(T) step prompts the question whether one might be able to substitute the small cc-pVDZ basis

set and still obtain useful results. Indeed, a composite of CCSD(T)-X2C/ACV5Z-X2C with CCSDT(Q)<sub>Λ</sub>/cc-pVDZ yields surprisingly good RMSD = 2.5 cm<sup>-1</sup> on harmonic frequencies and 0.001 Å on bond distances. This holds out a tantalising possibility for polyatomic molecules large enough that CCSDT(Q)<sub>Λ</sub>/cc-pVTZ would be cost-prohibitive.

### 3.3. The vibrational frequencies of ozone

It is clear from Figure 1 and Table 6 that the asymmetric (lambda-based) methods provide harmonic frequencies in better agreement with the corresponding fully iterative methods (such as CCSDT) than the more pragmatic symmetric approaches (like CCSD(T)). In this context, it is notable that CCSDT(Q)<sub>Λ</sub> agrees extremely well with the much more expensive CCSDTQ approach, while CCSDT(Q) fares slightly worse than CCSD(T). The latter's popularity can be viewed in this context as benefiting from an overestimation of triples effects, which partially compensates for the higher excitations that are neglected by these methods. This error compensation is familiar from computational thermochemistry (e.g. Refs. [4-9,18,19]), but is known there to break down beyond a certain level of static correlation. For instance, in Table S2 in Ref. [19], one finds the following post-CCSD(T) contributions to the ozone total atomisation energy: higher-order triples CCSDT



**Figure 1.** Harmonic vibrational frequencies of ozone at various levels of coupled cluster theory using the cc-pVDZ basis set, followed by a pictorial representation of the dependence of  $\omega_3$ . The CASSCF(18,12)-AQCC/cc-pVDZ result is shown schematically by the red line.

– CCSD(T) =  $-1.34$  kcal/mol, connected quadruples  $T_4 = +3.81$  kcal/mol, and connected quintuples  $T_5 = +0.41$  kcal/mol. By way of contrast, for a few representative molecules with less severe static correlation, error cancellation is seen to be largely preserved: for  $\text{CO}_2$ ,  $T_3$ -(T) =  $-1.03$ ,  $T_4 = +1.04$ , and  $T_5 = +0.05$  kcal/mol, and for  $\text{H}_2\text{O}_2$ :  $-0.55$ ,  $+0.72$ , and  $+0.03$  kcal/mol, respectively. From the point of view of formal theory, it is gratifying that the derivable lambda-based corrections [20–23] outperform the less theoretically justified symmetric methods (such as CCSD(T)). Nonetheless, it can be seen in Figure 1 and Table 6 that CCSD(T) and CCSDT(Q)<sub>Λ</sub> offer two ‘sweet spots’ within the coupled cluster series that accurately approximate the harmonic frequencies calculated by CCSDTQ5, a trend that was also observed for the diatomic test cases in the prior section. The reader should note that the  $T_5$  contribution to the asymmetric-stretching harmonic frequency is still  $16 \text{ cm}^{-1}$ , which might lead some reader to question whether it is truly a reliable estimate of full CI.

In an attempt at reaching the latter independently through a multireference approach, we carried out full valence CASSCF-AQCC calculations using MOLPRO 2022.3 [68]. As seen in Table 6, the corresponding harmonic frequencies agree to  $1 \text{ cm}^{-1}$  or better with CCSDTQ(5)<sub>Λ</sub>, and the geometry to the third decimal place (in Ångström).

Moreover, it can be seen in Table 6 that as the basis set is increased all the way to cc-pV5Z, the full valence CASSCF-AQCC calculations closely approach experiment.

Turning back to the cc-pVDZ basis set: replacing AQCC in the internally contracted multireference calculations by its direct ancestor ACPF (averaged coupled pair functional [47]) slightly degrades agreement with CCSDTQ(5)<sub>Λ</sub> (to  $2 \text{ cm}^{-1}$ ), but represents no fundamental departure. Replacing AQCC by MRCI (multireference configuration interaction) without a size-consistency correction increases differences to  $+9 \text{ cm}^{-1}$ ; inclusion of a Davidson-type size-consistency correction [41,42] reduces the discrepancy between CCSDTQ5(6) and CASSCF(18,12)-icMRCI+Q to  $1 \text{ cm}^{-1}$  or less for the frequencies, while the bond distance agrees to four significant figures. We also note in passing that the CAS(2,2)-MRCCSDT (multireference coupled cluster theory) results of Hanauer and Köhn are remarkably close to fully iterative CCSDTQ.

For the cc-pVTZ basis set, we were able to obtain at most CCSDT(Q)<sub>Λ</sub> frequencies, as well as those with lower-level approaches. In fact, with this basis set, the superiority of CCSDT(Q)<sub>Λ</sub> over CCSDT(Q) is even more obvious (Table 6). Owing to the same error compensation as for cc-pVDZ, CCSD(T) actually outperforms CCSDT(Q).

**Table 6.** Convergence of geometry (Å, degrees) and harmonic frequencies ( $\text{cm}^{-1}$ ) of ozone along the coupled cluster series.

	$\omega_1$ $a_1$	$\omega_2$ $a_1$	$\omega_3$ $b_2$	$r_{OO}$	$\theta$
cc-pVDZ					
CCSDTQ(5) $_{\Lambda}$	1072.6 $\Delta\omega_1$	687.8 $\Delta\omega_2$	990.8 $\Delta\omega_3$	1.29268 $\Delta r_{OO}$	116.217 $\Delta\theta$
CCSD	178.1	65.4	246.0	-0.03370	1.070
CCSD[T]	13.1	-1.9	-789.5	-0.00256	0.570
CCSD(T)	44.9	16.4	-14.1	-0.00828	0.424
CCSDT-1a	-19.8	-1.1	-303.1	0.00063	0.127
CCSDT-1b	9.7	6.0	88.9	-0.00213	0.202
CCSDT-2	70.8	25.0	178.7	-0.01133	0.394
CCSDT-3	62.7	19.4	114.1	-0.01013	0.490
CCSD(T) $_{\Lambda}$	72.4	24.8	69.8	-0.01235	0.571
CCSDT	53.9	17.7	74.1	-0.00927	0.272
CCSDT[Q]	19.4	8.0	50.2	-0.00340	0.069
CCSDT(Q)	-15.6	-5.6	-85.0	0.00217	-0.016
CCSDTQ-3	20.8	7.6	42.2	-0.00324	0.049
CCSDT(Q) $_{\Lambda}$	6.3	1.6	12.2	-0.00072	0.040
CCSDTQ	10.6	3.3	16.3	-0.00165	0.039
CCSDTQ[5]	-3.4	-0.5	-12.2	0.00035	-0.019
CCSDTQ(5)	-3.4	-0.5	-12.2	0.00035	-0.019
<b>CCSDTQ5</b>	<b>+0.3</b>	<b>+0.1</b>	<b>+1.6</b>	<b>-0.00003</b>	<b>+0.004</b>
CAS(18,12)-icAQCC	-1.1	-0.5	0.3	0.00077	-0.024
CAS(12,9)-icAQCC	1.6	1.8	0.5	-0.00073	0.016
CAS(18,12)-icACPF	-2.1	-1.4	-1.7	0.00118	-0.032
CAS(18,12)-icMRCI	3.4	3.9	9.2	-0.00144	0.024
CAS(18,12)-icMRCI+Q	0.2	0.3	-0.0	0.00008	-0.004
CAS(2,2)-MRCCSDT [48]	9.4	2.2	14.2	-0.00128	0.043
cc-pVTZ					
CAS(18,12)-icAQCC	1111.1 $\Delta\omega_1$	700.8 $\Delta\omega_2$	1058.9 $\Delta\omega_3$	1.28339 $\Delta r_{OO}$	116.541 $\Delta\theta$
CCSD(T)	42.0	14.9	-4.6	-0.00789	0.407
CCSDT	52.1	16.7	58.2	-0.00940	0.280
CCSDT[Q]	19.5	7.9	51.2	-0.00409	0.080
CCSDT(Q)	-17.0	-5.8	-87.2	0.00195	-0.037
CCSDT(Q) $_{\Lambda}$	3.3	0.6	7.3	-0.00070	0.017
cc-pVQZ					
CAS(18,12)-icAQCC	1129.4 $\Delta\omega_1$	710.5 $\Delta\omega_2$	1083.2 $\Delta\omega_3$	1.27626 $\Delta r_{OO}$	116.728 $\Delta\theta$
CCSD(T)	40.4	14.1	-2.0	-0.00745	0.390
CCSDT	51.0	16.0	53.3	-0.00903	0.274
CCSDT[Q]	18.5	7.5	49.6	-0.00392	0.076
cc-pV5Z					
CAS(18,12)-icAQCC	1133.9	713.0	1089.1	1.27460	116.760
Experiment [35,36]	1133.3(5)	714.9(4)	1087.2(3)	1.27276(15)	116.754(3)

We were alas unable to bring CCSDT(Q) $_{\Lambda}$ /cc-pVQZ calculations to completion, but Table 6 reveals that the deviations from CAS(18,12)-icAQCC of CCSD(T), CCSDT, and CCSDT[Q] are remarkably similar to those for the cc-pVTZ basis set, indicating that the latter have stabilised with respect to the basis set.

How well does full-valence CASSCF-AQCC perform for the diatomic test species of Subsection 3.1? We checked this for the cc-pVDZ basis set and found an RMSD with CCSDTQ5(6) of  $3.2 \text{ cm}^{-1}$ . This does include some cases such as  $\text{F}_2$ , ClF, and  $\text{Cl}_2$ , where a full-valence active space is inadequate as it only contains a single virtual orbital for these species; upon their removal or

recalculation with some added virtual orbitals, this can be reduced somewhat further. Suffice it to say that the gap is already small enough that we have further evidence for our CCSDTQ(5) $_{\Lambda}$  ozone frequencies being in error by *at most* a few wavenumbers. Thus, we recommend the CCSDTQ(5) $_{\Lambda}$  values to serve as a target of comparison for future benchmark calculations.

In fact, as the revision of this paper was being prepared for submission, fully iterative CCSDTQ5/cc-pVDZ calculations finally achieved convergence to the required precision after months of wall clock time. As shown in Table 6 at the bottom of the coupled cluster cc-pVDZ block, the differences with the CCSDTQ(5) $_{\Lambda}$  frequencies

are just +0.3, +0.1, and +1.6 cm<sup>-1</sup>, and in the geometry just -0.00003 Å and 0.004 degree. This further drives home the point that CCSDTQ(5)<sub>Λ</sub> is the next ‘Pauling point’ past CCSD(T) and CCSDT(Q)<sub>Λ</sub>.

#### 4. Conclusions

Our major conclusion for this dataset of diatomic spectroscopic constants is that within the coupled cluster series, and taking computational cost into account, CCSD(T) and CCSDT(Q)<sub>Λ</sub> emerge as two ‘sweet spots’ or Pauling points. In situations where static correlation is not too strong, CCSDT(Q) may be an acceptable alternative, with about one-half the memory demands and 2–3 shorter run times (owing to the elimination of the ‘left eigenvector’).

CCSD(T) being widely regarded as ‘the gold standard of quantum chemistry’ (a nickname first coined by Thom H. Dunning), perhaps CCSDT(Q)<sub>Λ</sub> may be considered the ‘platinum standard’, and CCSDTQ(5)<sub>Λ</sub> a ‘diamond standard’.

Finally, a composite of all-electron CCSD(T)-X2C/ACV5Z-X2C + [CCSDT(Q)<sub>Λ</sub> - CCSD(T)]/cc-pVTZ would appear to be a felicitous combination for computational vibrational spectroscopy, and a further cost reduction by substituting cc-pVDZ for cc-pVTZ does not greatly impair accuracy: RMSD( $\omega_e$ ) = increases from 2 to 2.5 cm<sup>-1</sup>. These combinations may prove especially useful for polyatomics.

#### Note

1. As ‘pentuple’ after ‘quadruple’ switches from Latin to Greek, the corresponding author prefers ‘quintuple’. Both notations can however be found in the literature.

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No potential conflict of interest was reported by the author(s).

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#### Data availability

Additional data can be obtained from the authors upon reasonable request.

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