The convergence of the coupled cluster approach for MgO

Charles W. Bauschlicher, Jr.*

NASA Ames Research Center, Moffett Field, CA 94035

Abstract

The $X^1\Sigma^+$ state of MgO shows significant differences between the CCSD(T) and CCSDT results and even some significant differences between the CCSDT and CCSDTQ results. The CCSDT(Q) results for this state do not agree well with the CCSDTQ results. Unlike the X state, the $a^3\Pi$ state, which is well described by a single configuration, shows much less dependence on level of correlation treatment. Despite the slow convergence of the valence treatment of the X state, the effect of core correlation converges rapidly with level of correlation treatment.

Keywords: CCSD(T), CCSDT, CCSDTQ, core correlation

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* Mail Stop 230-3, Thermal Protection Materials Branch, Charles.W.Bauschlicher@nasa.gov

I. INTRODUCTION

We recently studied[1] the spectra of MgO using a dynamical weighted state-averaged complete active space self-consistent-field/internally contracted multireference configuration interaction (DW-SA-CASSCF/IC-MRCI) approach[2,3]. To make the study of 25 electronic states practical, we only correlated the valence electrons. As part of this study, we considered effect of core correlation on some of the properties $(r_e, \omega_e, T_e, \text{ and } D_e)$ of the two lowest states, namely, the $X^1\Sigma^+$ and $a^3\Pi$ states, using the coupled cluster singles and doubles with a perturbative estimate for the triples, i.e. CCSD(T)[4,5] approach. At the valence level, the CCSD(T) and IC-MRCI r_e and ω_e results for the $a^3\Pi$ state were in very good agreement, while the CCSD(T) and IC-MRCI results for the $X^1\Sigma^+$ state did not agree with experiment as well as for the a state. This is consistent with the multireference character of the $X^1\Sigma^+$ state, and suggests that one must go beyond the CCSD(T) approach to obtain more accurate results for the X state. We should note however, that while the CCSD(T) and IC-MRCI r_e, ω_e, and T_e results differed, the effect of core correlation computed at the CCSD(T) level was similar to the difference between the IC-MRCI and experiment. Thus suggesting that the CCSD(T) approach might give a good estimate for the core correlation, even though the valence results were disappointing.

Consistent with our findings on MgO, Martin and co-workers have found[6–8] that to obtain extremely accurate thermochemistry, it is often necessary to use higher levels of coupled cluster theory than CCSD(T). For example, they considered coupled cluster theory including triples and quadruples, CCSDT and CCSDTQ, and a version where the quadruples were included perturbatively, CCSDT(Q). We should note that in their study, they also found MgO $X^1\Sigma^+$ to be one of the more difficult systems to describe.

In this work, we return to the $X^1\Sigma^+$ and the $a^3\Pi$ states of MgO and study the effect of going beyond CCSD(T) on the properties of these two states, one of which is well described by a single configuration and the other, which is not. We consider treatments that include valence and core+valence correlation.

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II. METHODS

The $X^1\Sigma^+$ state is a closed-shell system and a spin-restricted Hartree-Fock (RHF) reference is used in all calculations. The $a^3\Pi$ state is an open-shell system and both spin-restricted (RHF) and spin-unrestricted HF (UHF) based approaches are used. Several levels of coupled cluster calculations are performed. The simplest approach is the CCSD(T)[4,5]. For the $a^3\Pi$ state, the RHF based approach is the RCCSD(T) described by Knowles et al.[9], while the UHF based approach is the usual UCCSD(T) method. The next level is the CCSDT approach[10] that includes the triples iteratively. The CCSDT(Q) includes a perturbative estimate of the quadruples[11]. Our final level, CCSDTQ, includes the quadruples iteratively[12]. We correlate the valence electrons, i.e. the Mg $3s$ and oxygen $2s$ and $2p$ electrons in our valence treatment and all electrons except the Mg $1s$ electrons in our core+valence treatment.

The correlation consistent basis sets developed by Peterson and Dunning and their co-workers[13–16] are used in all calculations. The valence correlation treatment uses augmented-correlation-consistent polarized valence triple zeta (aug-cc-pVTZ), quadruple zeta (aug-cc-pVQZ) and quintuple zeta (aug-cc-pV5Z) basis sets. To study the effect of core correlation, the correlation-consistent polarized core-valence (cc-pCV) basis sets are used; the same basis sets are used for valence and core+valence calculations so the core correlation effects can be computed without any complications from the use of different basis sets. Test calculations show that the diffuse functions on Mg have virtually no effect on the results, which is consistent with the $Mg^{2+}O^{2-}$ or Mg^+O^- character of the states. Therefore, the augmented functions are only added to the oxygen atom in these calculations. We use the double zeta, triple zeta, quadruple zeta, and quintuple zeta versions of these basis sets. That is, we use the aug-cc-pCVDZ, aug-cc-pCVTZ, aug-cc-pCVQZ, and aug-cc-pCV5Z sets for oxygen and the cc-pCVDZ, cc-pCVTZ, cc-pCVQZ, and cc-pCV5Z sets for Mg. We denote these basis sets as (aug)-cc-pCVnZ, where the aug is in parentheses to indicate that the diffuse functions are only added to the oxygen atom.

We test the effect of relativity using the Douglas-Kroll approximation[17,18]. The CCSD(T) (X state) and RCCSD(T) (a state) approaches are used in conjunction

with aug-cc-pVTZ-DK basis sets. As we show below, the effect of relativity is very small on the properties considered in this work, and therefore most of the calculations ignore relativistic effects.

The geometries were optimized and harmonic frequencies were computed using a parabolic fit in r and $1/r$. The points used in the fit are r_e and $r_e \pm 0.01$ or $r_e \pm 0.02$ Å. Tests show that the bond lengths should be accurate to about 0.001 Å and the T_e values to about 1 cm^{-1}. While the ω_e values computed using the r and $1/r$ agree to better than 1 cm^{-1}, varying the spacing between the points can lead to differences of a few cm^{-1}. Therefore in the tables, variations in the ω_e values should be given much less weight than changes in r_e and T_e.

The $X^1\Sigma^+$ CCSD(T) calculations and $a^3\Pi$ RCCSD(T) calculations are performed using MOLPRO[19]. The $a^3\Pi$ RCCSDT calculations are performed using MOLPRO interfaced with the MRCC program[20]. All of the other calculations are performed using the MRCC program, except for the $X^1\Sigma^+$ CCSD(T) and $a^3\Pi$ UCCSD(T) calculations in the (aug)-cc-pCV5Z basis set which are performed using Gaussian16[21].

III.   RESULTS AND DISCUSSION

The results of the valence level treatments are summarized in Table I. The top two entries compare CCSD(T) calculations with and without relativistic corrections. The r_e values are unchanged and the T_e and ω_e values are hardly changed. Clearly relativistic effects make a small difference on the properties considered in this work and are therefore ignored in the rest of the calculations.

The r_e and ω_e values for the $a^3\Pi$ state do not strongly depend on the level of correlation treatment used. For the aug-cc-pVTZ basis set, the r_e value varies by 0.002Å with correlation method, while the ω_e value varies by about 3 cm^{-1}. Improving the basis set, reduces the r_e value and increases the ω_e value; the difference between the UCCSDT values in aug-cc-pVTZ and aug-cc-pV5Z basis sets are 0.011 Å and 10.8 cm^{-1}, respectively. That is, the change with basis set is five times larger than that found for changing the level of correlation treatment. For the $X^1\Sigma^+$ state, the variation with level of correlation treatment is about the same size as the vari-

ation with basis set. That is, the $X^1\Sigma^+$ state is much more sensitive to the level of correlation treatment, which is consistent with the fact that the X state is not as well described by a single configuration as the a state. Given the fact that the two states are not equally well described by a single reference, it is not surprising that the T_e value is sensitive to the correlation treatment.

For the X state the CCSDT and CCSD(T) results shows some significant differences; the CCSDT has a longer bond length and smaller ω_e value than does the CCSD(T). Also note the change in T_e between these two methods. While difference in the r_e and ω_e values between the CCSDT and CCSDTQ are smaller than found between the CCSD(T) and CCSDT, the T_e value show a surprisingly large effect; see the results for the aug-cc-pVTZ basis set in Table I. Given that the X state is not well described by a single configuration, it is not unexpected that the perturbative and iterative description of triples differ. However, it somewhat disappointing that the CCSDT(Q) T_e values do not agree well with that obtained at the CCSDTQ level. We further note that CCSDT(Q) suggest the quadruples increases r_e by 0.002 Å and decreases ω_e by 10.7 cm^{-1}, while the CCSDTQ shows an increase of 0.001 Å r_e and an increase of 2.3 cm^{-1} in ω_e.

Our highest level calculation is the CCSDT/aug-cc-pV5Z approach. For the $a^3\Pi$ state this level yields r_e and ω_e values are in excellent agreement with our previous results[1] using the IC-MRCI approach in conjunction with the same basis set, see Table I. The X state shows somewhat larger differences between the two methods, but CCSDT is a very large improvement over the CCSD(T) approach. The IC-MRCI T_e value is actually closer to the CCSD(T) result then the CCSDT value. The CCSDTQ results in the TZ basis set suggests that the CCSD(T) is benefitting from a cancelation of errors as the inclusion of quadruples would increase the CCSDT value by more than 500 cm^{-1}. The CCSDT value can be improved by extrapolating[22] to the complete basis set (CBS) limit and adding on an estimate for the effect of quadruples using the aug-cc-pVTZ basis set, namely

$$\text{CCSDT/CBS} + \text{CCSDTQ/aug-cc-pVTZ} - \text{CCSDT/aug-cc-pVTZ},$$

which is denoted "CBS+Q(TZ)" in the table. This estimate is compared with experiment[23] in Table I. Note that we also give the CCSDT/aug-cc-pV5Z values to show

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the size of the CBS extrapolation. Our best valence estimates differ from experiment. Since we showed relativistic effects are small, the difference with experiment probably arises from core-correlation, and we therefore next consider this effect.

The results including core correlation are shown in Table II, along with the valence results obtained using the same basis set. The agreement of the valence treatments using the aug-cc-pVnZ and (aug)-cc-pCVnZ basis set is very good. While the tight functions added to the aug-cc-pVnZ basis set to form the (aug)-cc-pCVnZ sets are added for inner shell correlation, they have have some effect on the valence results, in this regard, we note that (aug)-cc-pCVTZ results fall between those obtained using the (aug)-cc-pVTZ and (aug)-cc-pVQZ sets.

The results obtained in the bottom of the table include core correlation. The trends with basis set improvement and level of correlation treatment follow those discussed above for the valence treatment. Of more interest is the effect of the core correlation, and these results are summarize in Table III, which are obtained by taking the difference between the valence and core+valence results obtained using the (aug)-cc-pCVnZ basis sets; that is, as differences between the results in the top and bottom of Table II. While the effect of core correlation increases with basis set improvement, for a given basis set, the effect of core correlation are much less dependent on the level of correlation than are the values themselves. For example the difference between the CCSD(T) and CCSDTQ T_e values in the (aug)-cc-pCVDZ basis set is only about 17 cm^{-1}. Since the CCSD(T) and CCSDT T_e values approximately double between the (aug)-cc-pCVDZ and (aug)-cc-pCVQZ basis sets, the effect of the quadruples is probably underestimated using the (aug)-cc-pCVDZ basis set, but it is safe to conclude that the effect of quadruples is small. This is encouraging as it is then possible to correct high level valence treatment for core effects using lower levels of theory.

Our best valence level results show some significant differences with experiment as did our previous IC-MRCI results. This suggest that most of the difference with experiment is due to core correlation. However, the additional electrons to be correlated, means that the inclusion of triples and quadruples must be performed in smaller basis sets than for the valence treatment. This means that our best estimate will have to

a composite of several treatments. We take our CCSDT/(aug)-cc-pCVQZ results as our best directly computed values for the effect of core correlation. This value should be corrected for basis set incompleteness and higher level correlation. The basis set incompleteness can be estimated as the difference between the CCSD(T)/RCCSD(T) or CCSD(T)/UCCSD(T) levels using the (aug)-cc-pCVQZ and (aug)-cc-pCV5Z basis sets. Since the CCSDT/(aug)-cc-pCVQZ core calculations are very expensive, we also try using the CCSDT/(aug)-cc-pCVTZ results with a basis set correction computed using the CCSD(T) values for the (aug)-cc-pCVTZ and (aug)-cc-pCV5Z basis sets. Higher excitations can be estimated using the CCSDTQ and CCSDT results performed with the (aug)-cc-pCVDZ set; this suggests that quadruples increase T_e by 15 cm^{-1} and has virtually no effect on the other properties. Since the CCSD(T)/(aug)-cc-pCVDZ yields about half the core effect as CCSD(T)/(aug)-cc-pCV5Z, we double the T_e value computed using the smaller basis set, and conclude that quadruples would increase T_e by about 30 cm^{-1}.

We add our estimates for the core correlation effects to our best estimate for the valence results to obtain our best estimates; these results are summarized in Table IV. For comparison, our valence estimates are included in the top of the table and experiment at the bottom. We first note that using the RCCSD(T) or UCCSD(T) approach to estimate the basis set incompleteness yields very similar results. In addition, using the smaller CCSDT/(aug)-cc-pCVTZ result corrected with CCSD(T)(5Z-TZ) estimate for core correlation basis set incompleteness, instead of the CCSDT/(aug)-cc-pCVQZ + CCSD(T)(5Z-QZ), makes a very small difference. This is very encouraging as the CCSDT/(aug)-cc-pCVTZ is significantly cheaper than the CCSDT/(aug)-cc-pCVQZ calculation. It is also interesting to note that just using the CCSD(T)/(aug)-cc-pCV5Z approach, without any CCSDT calculations gives a good estimate for the core correlation. That is, while the CCSD(T) approach is not sufficient for the valence description of the X state, it does give a reasonable estimate for the core effects. All of the results including a estimate for the core correlation are in reasonable agreement with experiment.

All of the results using CCSDT/CBS+Q for the valence result and the CCSDT based results for the core effect have about a 30 cm^{-1} error in the T_e value. This

increases a bit if the CCSDT/5Z+Q is used for the valence or if only the CCSD(T) approach is used from the core contribution, but all are a big improvement over the valence result. The a state r_e value agrees with experiment if the CBS based result is used and slightly long if the 5Z based result is used. The 5Z based X state r_e value is slightly too long while the CBS yields a r_e value that is too short, but both values significantly better than the valence results. Because of the uncertainty in the ω_e values, it is harder to make any definitive statements other than that all of the methods give reasonable results, and the values for the X state are an improvement on the valence results.

IV. CONCLUSIONS

The CCSD(T), CCSDT, and CCSDTQ results for the $a^3\Pi$ state are in good agreement, as expected for a state well described by a single reference configuration. For the $X^1\Sigma^+$ state, which is not as well described by a single reference configuration, the CCSDT and CCSD(T) results differ. For this state, there is also a significant difference between the CCSDT and CCSDTQ. The CCSDT(Q) results differ with those obtained using the CCSDTQ. Unlike the valence treatment, it appears that there is a cancellation of errors such that the effect of core correlation is much easier to describe. Even the CCSD(T) approach gives a reasonable result for effect of core correlation. This is encouraging for composite methods of computing properties as adding core correlation can dramatically increase the cost of the calculation.

V. ACKNOWLEDGMENTS

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TABLE I: Summary of spectroscopic constants for the valence treatment of correlation.

$X^1\Sigma^+$			$a^3\Pi$			
Method	r_e(Å)	ω_e(cm^{-1})	Method	r_e(Å)	ω_e(cm^{-1})	T_e(cm^{-1})
			aug-cc-pVTZ-DK			
CCSD(T)-DK	1.766	769.1	RCCSD(T)-DK	1.894	632.2	1687.6
CCSD(T)	1.766	771.5	RCCSD(T)	1.894	633.7	1679.9
			aug-cc-pVTZ			
CCSD(T)	1.766	770.4	RCCSD(T)	1.895	632.9	1677.6
			UCCSD(T)	1.895	634.9	1608.0
CCSDT	1.777	753.8	RCCSDT	1.896	633.3	1340.2
			UCCSDT	1.896	632.7	1321.2
CCSDT(Q)	1.779	743.1	UCCSDT(Q)	1.896	631.5	2182.0
CCSDTQ	1.778	756.1	UCCSDTQ	1.896	631.9	1860.5
			aug-cc-pVQZ			
CCSD(T)	1.759	788.5	RCCSD(T)	1.888	642.8	1864.5
CCSDT	1.770	763.1	RCCSDT	1.889	641.0	1487.1
			UCCSDT	1.889	640.4	1466.2
CCSDT(Q)	1.772	752.7	UCCSDT(Q)	1.889	639.2	2335.0
			aug-cc-pV5Z			
CCSD(T)	1.755	796.9	RCCSD(T)	1.884	645.8	1999.5
CCSDT	1.765	765.5	UCCSDT	1.885	643.5	1571.2
CCSDT(Q)	1.768	756.9	UCCSDT(Q)	1.885	642.3	2439.7
IC-MRCI[1]	1.769	768.6	IC-MRCI[1]	1.884	643.7	1932.8
			Best Estimates			
5Z+Q(TZ)	1.766	767.7		1.885	642.7	2110.5
CBS+Q(TZ)	1.762	770.2		1.881	646.0	2220.7
Expt	1.749	785.0		1.868	650.2	2621.0

TABLE II: Summary of spectroscopic constants for valence and core treatment of correlation.

	$X^1\Sigma^+$			$a^3\Pi$		
Method	r_e(Å)	ω_e(cm^{-1})	Method	r_e(Å)	ω_e(cm^{-1})	T_e(cm^{-1})
			Valence correlation			
			(aug)-cc-pCVDZ			
CCSD(T)	1.782	751.1	RCCSD(T)	1.908	624.9	943.3
CCSDT	1.793	740.8	UCCSDT	1.910	621.1	759.1
CCSDTQ	1.794	743.1	UCCSDTQ	1.910	620.3	1240.6
			(aug)-cc-pCVTZ			
CCSD(T)	1.760	783.6	RCCSD(T)	1.890	636.5	1795.3
			UCCSD(T)	1.890	635.7	1722.8
CCSDT	1.771	756.4	RCCSDT	1.891	633.7	1382.4
			UCCSDT	1.891	633.5	1402.4
CCSDT(Q)	1.773	746.1	UCCSDT(Q)	1.891	632.3	2261.0
			(aug)-cc-pCVQZ			
CCSD(T)	1.755	797.3	RCCSD(T)	1.884	644.9	1973.2
			UCCSD(T)	1.884	644.2	1898.5
CCSDT	1.766	765.3	UCCSDT	1.885	643.2	1548.1
			(aug)-cc-pCV5Z			
CCSD(T)	1.754	798.5	RCCSD(T)	1.883	650.9	2027.4
			UCCSD(T)	1.883	645.1	1953.0
			Core+Valence correlation			
			(aug)-cc-pCVDZ			
CCSD(T)	1.774	757.3	RCCSD(T)	1.903	617.5	1125.2
CCSDT	1.786	744.1	UCCSDT	1.905	619.1	942.3
CCSDTQ	1.786	746.0	UCCSDTQ	1.906	618.2	1439.2
			(aug)-cc-pCVTZ			
CCSD(T)	1.748	796.2	RCCSD(T)	1.880	640.2	2088.5
			UCCSD(T)	1.881	639.3	2031.4
CCSDT	1.759	765.2	RCCSDT	1.882	637.1	1694.9
			UCCSDT	1.882	637.1	1694.9
CCSDT(Q)	1.760	757.0	UCCSDT(Q)	1.882	635.7	2590.2
			(aug)-cc-pCVQZ			
CCSD(T)	1.741	811.8	RCCSD(T)	1.872	648.8	2298.7
			UCCSD(T)	1.873	649.7	2239.6
CCSDT	1.751	777.7	UCCSDT	1.873	648.7	1873.1
			(aug)-cc-pCV5Z			
CCSD(T)	1.739	814.5	RCCSD(T)	1.870	652.6	2368.3
			UCCSD(T)	1.870	651.6	2309.2

TABLE III: The effect of core correlation.

	$X^1\Sigma^+$			$a^3\Pi$		
Method	r_e(Å)	ω_e(cm^{-1})	Method	r_e(Å)	ω_e(cm^{-1})	T_e(cm^{-1})
			(aug)-cc-pCVDZ			
CCSD(T)	-0.008	6.2	RCCSD(T)	-0.005	-7.4	181.9
CCSDT	-0.008	3.4	UCCSDT	-0.005	-2.0	183.2
CCSDTQ	-0.008	2.9	UCCSDTQ	-0.004	-2.2	198.6
			(aug)-cc-pCVTZ			
CCSD(T)	-0.012	12.6	RCCSD(T)	-0.009	3.7	293.3
			UCCSD(T)	-0.009	3.6	308.5
CCSDT	-0.012	8.8	RCCSDT	-0.009	3.4	312.5
			UCCSDT	-0.009	3.6	292.5
CCSDT(Q)	-0.013	10.9	UCCSDT(Q)	-0.009	3.5	329.2
			(aug)-cc-pCVQZ			
CCSD(T)	-0.014	14.4	RCCSD(T)	-0.012	3.9	325.5
			UCCSD(T)	-0.011	5.5	341.0
CCSDT	-0.015	12.5	UCCSDT	-0.011	5.5	325.1
			(aug)-cc-pCV5Z			
CCSD(T)	-0.015	16.0	RCCSD(T)	-0.013	1.6	340.8
			UCCSD(T)	-0.013	6.5	356.1

TABLE IV: Best estimates for the spectroscopic constants. r_e is in Å and ω_e and T_e are in cm^{-1}.

Method		$X^1\Sigma^+$		$a^3\Pi$		
Valence[a]	Core[b]	r_e	ω_e	r_e	ω_e	T_e
5Z+Q(TZ)		1.766	767.7	1.885	642.7	2110.5
CBS+Q(TZ)		1.762	770.2	1.881	646.0	2220.7
5Z+Q(TZ)	QZ+RCCSD(T)(5Z-QZ)+Q(DZ)*2	1.751	781.8	1.872	646.0	2480.9
5Z+Q(TZ)	QZ+UCCSD(T)(5Z-QZ)+Q(DZ)*2	1.751	781.8	1.872	649.2	2480.7
5Z+Q(TZ)	TZ+RCCSD(T)(5Z-TZ)+Q(DZ)*2	1.751	779.9	1.872	644.3	2480.7
5Z+Q(TZ)	TZ+UCCSD(T)(5Z-TZ)+Q(DZ)*2	1.751	779.9	1.872	649.2	2480.6
CBS+Q(TZ)	QZ+RCCSD(T)(5Z-QZ)+Q(DZ)*2	1.746	784.3	1.868	649.3	2591.1
CBS+Q(TZ)	QZ+UCCSD(T)(5Z-QZ)+Q(DZ)*2	1.746	784.3	1.868	652.5	2590.9
CBS+Q(TZ)	TZ+RCCSD(T)(5Z-TZ)+Q(DZ)*2	1.746	782.3	1.868	647.6	2590.8
CBS+Q(TZ)	TZ+UCCSD(T)(5Z-TZ)+Q(DZ)*2	1.746	782.3	1.868	652.5	2590.8
5Z+Q(TZ)	RCCSD(T)(5Z)+Q(DZ)*2	1.751	783.8	1.872	644.4	2451.4
5Z+Q(TZ)	UCCSD(T)(5Z)+Q(DZ)*2	1.751	783.8	1.872	649.3	2466.7
CBS+Q(TZ)	RCCSD(T)(5Z)+Q(DZ)*2	1.746	786.2	1.868	647.6	2561.6
CBS+Q(TZ)	UCCSD(T)(5Z)+Q(DZ)*2	1.746	786.2	1.868	652.5	2576.8
Expt		1.749	785.0	1.868	650.2	2621.0

[a] "5Z" denotes the CCSDT/aug-cc-pV5Z results and +Q(TZ) denotes the effect for quadruples compute as the difference between the CCSDTQ and CCSDT in the aug-cc-pVTZ basis set. "CBS" indicates the CCSDT is extrapolated complete basis set limit.

[b] "QZ" denotes the core effect computed using the CCSDT/(aug)-cc-pCVQZ approach, while "TZ" indicates the analogous result from (aug)-cc-pCVTZ basis set. The (R or U) CCSD(T)(X,Y) indicates that the CCSD(T) and (R or U)CCSD(T) approach using the X and Y basis sets where used to estimate the basis incompleteness for the core correlation. "(R or U) CCSD(T)(5Z)" indicates the effect of core correlation is computed using the (R or U)CCSD(T)/(aug)-cc-pCV5Z basis set. "Q(DZ)" indicates the effect of quadruples in the (aug)-cc-pCVDZ basis set.