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CCSDT calculations of molecular equilibrium geometries

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Abstract

CCSDT equilibrium geometries of CO, CH₂, F₂, HF, H₂O and N₂ have been calculated using the correlation-consistent cc-pVXZ basis sets. Similar calculations have been performed for SCF, CCSD and CCSD(T). In general, bond lengths decrease when improving the basis set and increase when improving the *N*-electron treatment. CCSD(T) provides an excellent approximation to CCSDT for bond lengths as the largest difference between CCSDT and CCSD(T) is 0.06 pm. At the CCSDT/cc-pVQZ level, basis set deficiencies, neglect of higher-order excitations, and incomplete treatment of core-correlation all give rise to errors of a few tenths of a pm, but to a large extent, these errors cancel. The CCSDT/cc-pVQZ bond lengths deviate on average only by 0.11 pm from experiment. © 1997 Elsevier Science B.V.

1. Introduction

During the last decade, the coupled cluster method has been recognized as the most efficient way of describing dynamical correlation effects for systems dominated by a single reference configuration. The coupled cluster singles and doubles (CCSD) model [1] is the simplest and most commonly used model in the coupled cluster hierarchy. CCSD includes the effects of all single and double excitations out of the reference configuration, which is usually chosen as the Hartree–Fock self-consistent-field (SCF) wavefunction. At the next level of theory, triple excitations are included, resulting in the CCSDT model [2]. This model is computationally demanding, however, scaling as N^8 , where N is the number of basis functions. For comparison, the CCSD model scales as N^6 . Therefore, a variety of models with an approximate treatment of triple excitations (all scaling as N^7) have been introduced. Among these, the

CCSD(T) model [3] has proved to be the most successful.

The CCSD(T) model has been used to calculate a variety of molecular properties such as nuclear shielding tensors [4] and equilibrium geometries [5], with an accuracy that is comparable to and sometimes surpasses that of experiment. The overall excellent agreement with experiment may, however, arise from a fortuitous cancellation of the errors arising from the incomplete treatments of the one- and *N*-electron spaces. To investigate the quality of the CCSD(T) model closer, it is necessary to carry out calculations at a higher level of correlation. In particular, by carrying out calculations at the CCSDT level for a few selected systems, it should be possible to separate the errors in the CCSD(T) model that arise from the approximate treatment of the triple excitations from those errors that arise from the neglect of higher-order excitations and from basis set truncation (i.e., from those errors that are also pre-

sent in the CCSDT model). Obviously, although the CCSDT model itself is too expensive for routine work, it is of interest to compare CCSDT results with experiment. The CCSDT correlation treatment is a highly sophisticated one and, in a sufficiently large basis, this model should yield results in close agreement with experiment.

In this paper, we present systematic calculations of equilibrium geometries of the six molecules CO, CH₂, F₂, HF, H₂O and N₂ at the SCF, CCSD, CCSD(T) and CCSDT levels of theory, using the correlation-consistent basis sets cc-pVXZ developed by Dunning and coworkers [6]. These basis sets constitute excellent hierarchies of one-electron basis sets, providing a systematic convergence towards the basis set limit. In our discussions, special attention is paid to the results obtained at the CCSD(T) and CCSDT levels, comparing these with each other and also with experiment. In these calculations the full set of core and valence electrons are correlated, even though basis sets developed only for valence correlation are used. This approach may be considered somewhat unsatisfactory and it might be argued that one should either (1) correlate only the valence electrons in the valence basis sets cc-pVXZ or (2) correlate all the electrons in the correlation-consistent core-valence basis sets cc-pCVXZ (also developed by Dunning and coworkers) [7]. However, the two approaches were impossible because of current limitations in the software and hardware respectively. We have, however, considered the effects of core correlation in more detail at the second-order Møller-Plesset (MP2) level of theory [10], presenting calculations at the cc-pV5Z and cc-pCV5Z levels in order to investigate the effect of core-correlation and in particular the errors that arise from the lack of core-correlating functions in the cc-pVXZ basis sets.

2. Computational details

For all the wave functions, SCF, CCSD, CCSD(T) and CCSDT, we have carried out calculations using the cc-pVDZ, cc-pVTZ and cc-pVQZ basis sets. In addition, we have carried out calculations at the cc-pV5Z level for the wave functions SCF, CCSD and CCSD(T). All these calculations have been per-

formed using the acesii program [8,9]. For the CCSDT wave function, the molecular gradient needed for the optimization was obtained by numerical differentiation of the electronic energy since analytical gradients have not yet been implemented at this level of theory.

To investigate the effect of core-correlation, we have carried out three sets of calculations at the MP2 level of theory: (1) one set with all the electrons correlated in the cc-pCV5Z basis set, (2) one set with all the electrons correlated in the cc-pV5Z basis set and (3) one set with only the valence electrons correlated in the cc-pV5Z basis set. These calculations were carried out using the Gaussian 94 program package [11], which has the option to perform geometry optimizations with the core electrons frozen.

3. Results

3.1. The dependence of bond distances on basis sets and correlation treatment

In Tables 1 and 2, the equilibrium bond distances (r_e) obtained for the six molecules using the SCF, CCSD, CCSD(T) and CCSDT wave functions are listed. In accordance with the observations of Helgaker et al. in Ref. [5], we find in general that the

Table 1
Calculated r_e in pm in the N₂, CO and F₂ molecules

	SCF	CCSD	CCSD(T)	CCSDT
N_2				
cc-pVDZ	107.730	111.232	111.842	111.798
cc-pVTZ	106.711	109.363	110.059	109.998
cc-pVQZ	106.558	109.089	109.809	109.746
cc-pV5Z	106.541	108.953	109.678	
CO				
cc-pVDZ	111.014	113.792	114.413	114.435
cc-pVTZ	110.446	112.562	113.247	113.237
cc-pVQZ	110.199	112.187	112.891	112.877
cc-pV5Z	110.183	112.015	112.724	
F_2				
cc-pVDZ	134.765	143.184	145.751	145.762
cc-pVTZ	132.913	139.230	141.360	141.329
cc-pVQZ	132.747	138.855	141.112	141.075
cc-pV5Z	132.667	138.589	140.882	

Table 2
Calculated r_e in pm in the HF, H_2O and CH_2 molecules

	SCF	CCSD	CCSD(T)	CCSDT
HF				
cc-pVDZ	90.149	91.866	91.959	91.967
cc-pVTZ	89.794	91.412	91.618	91.618
cc-pVQZ	89.690	91.261	91.517	91.516
cc-pV5Z	89.696	91.267	91.547	
H_2O				
cc-pVDZ	94.629	96.435	96.575	96.584
cc-pVTZ	94.060	95.551	95.782	95.779
cc-pVQZ	93.960	95.358	95.623	95.620
cc-pV5Z	93.957	95.357	95.639	
CH_2				
cc-pVDZ	110.707	112.684	112.801	112.799
cc-pVTZ	109.569	110.279	110.423	110.404
cc-pVQZ	109.463	110.356	110.517	110.499
cc-pV5Z	109.436	110.175	110.342	

bond distances decrease with improvements in the basis sets and increase with improvements in the N -electron treatment. More specifically, we find that the bond distances increase in the order SCF < CCSDT/CCSD(T) and that the CCSD(T) bond lengths (beyond the cc-pVDZ level at least) are slightly longer than the CCSDT bonds.

Concerning the basis set dependence, we note that the bonds invariably contract as we go from cc-pVDZ to cc-pVTZ with the following average contractions: HF 0.92 pm; CCSD 1.80 pm; CCSD(T) 1.81 pm; CCSDT 1.83 pm. The contractions are thus about 1 pm at the uncorrelated level and about 2 pm at the correlated levels. Beyond the cc-pVTZ level, the situation is less clear-cut and in some cases the bond lengths are found to increase with extensions of the basis set. In the HF molecule, for example, the bond length increases as we go from cc-pVQZ to cc-pV5Z. Similarly, there is a slight increase in the OH bond length of H_2O as we go from cc-pVQZ to cc-pV5Z, but only at the CCSD(T) level. Finally, the CH bond length in CH_2 increases as we go from cc-pVTZ to cc-pVQZ except at the Hartree–Fock level. It should be noted, however, that the changes in the bond lengths between cc-pVTZ and cc-pVQZ and between cc-pVQZ and cc-pV5Z are significantly smaller than the contractions observed from cc-pVDZ to cc-pVTZ. Thus, at the CCSD(T) level, the mean absolute changes in the bond distances from cc-pVTZ to cc-pVQZ and from cc-pVQZ to cc-pV5Z are 0.20

and 0.12 pm, respectively — considerably smaller than the change of 1.81 pm observed between cc-pVDZ and cc-pVTZ.

3.2. CCSD(T) and CCSDT bond distances compared

From Tables 1 and 2, we see that the CCSDT and CCSD(T) bond lengths are very similar — the largest difference being 0.06 pm for N_2 in cc-pVQZ. We also note that, except for the (inadequate) cc-pVDZ basis, the CCSD(T) bonds are always slightly longer than the CCSDT bonds. The effects of triple excitations are thus slightly overestimated by the CCSD(T) model — by as little as 0.4% in HF and by as much as 9.6% in N_2 . In general, the CCSD(T) model provides an excellent approximate description of the effect of triple excitations on the bond distances, at least for molecules containing first-row atoms only.

One might speculate that the ability of the CCSD(T) model to provide an accurate representation of the triples effects on the bond distances should be related to the total correlation contribution to the bond distances in such a manner that bonds with overall large correlation corrections should be most affected by the approximations made in the CCSD(T) model. This is not the case, however. In fact, for the two molecules in our study with the smallest and largest correlation corrections to the bond lengths (i.e., CH_2 with a correction of 1.0 pm and F_2 with a correction of 8.3 pm from SCF/cc-pVQZ to CCSDT/cc-pVQZ), the CCSD(T) model overestimates the triples correction by exactly the same amount (1.7%).

The differences between the CCSDT and CCSD(T) bond distances are very nearly the same at the cc-pVTZ and cc-pVQZ levels, differing by only –0.001 to 0.006 pm. It is therefore possible to estimate a CCSDT/cc-pVQZ bond length to within 0.01 pm from the bond length at the CCSD(T)/cc-pVQZ level and the difference between CCSDT and CCSD(T) and the cc-pVTZ level. A similar estimate of the full triples correction based on the differences between CCSD and CCSDT is not possible since these (much larger) corrections differ considerably between the cc-pVTZ and cc-pVQZ basis sets (the F_2 bond-length correction differing by as much as 0.12 pm).

3.3. Comparison with experiment

Calculations where the errors arising from truncations in the one-electron space are of the same magnitude as those arising from approximations made in the N -electron space, are often referred to as “balanced”. In balanced calculations, there are no lost efforts in the sense that further improvements require improvements in both the one-electron and the N -electron descriptions.

For the calculation of molecular bond distances we have seen, that the errors arising from basis set truncations and from approximations in the correlation treatment are usually oppositely directed. Balanced calculations of bond distances therefore tend to give bond distances in good agreement with experiment. Such an example is provided by the CCSDT/cc-pVQZ level, where the results are in excellent agreement with the experimentally deduced bond distances: The small higher-order correlation effects are almost cancelled by the remaining basis set errors — see columns two and four in Table 3, where we compare the CCSDT/cc-pVQZ bond distances with experiment. The mean absolute deviation from experiment is $|\bar{\Delta}|_{\text{CCSDT/cc-pVQZ}} = 0.11$ pm, with a maximum deviation of 0.2 pm (CH_2). Except for CO, the calculated bonds are shorter than experiment. Since the CCSD(T) bonds are slightly longer than those at the CCSDT level, the agreement with experiment is even better for CCSD(T)/cc-pVQZ than for CCSDT/cc-pVQZ. The mean absolute deviation from experiment at the CCSD(T)/cc-pVQZ level is $|\bar{\Delta}|_{\text{CCSD(T)/cc-pVQZ}} = 0.10$ pm, the maxi-

mum deviation is 0.2 pm (CH_2), and two bonds (CO and N_2) are now longer than experiment.

At the CCSD(T)/cc-pVQZ level, the deviation from experiment is seen to be of the same magnitude as the basis set error (0.12 pm as measured by the change from cc-pVQZ to cc-pV5Z), but, since an increase in the basis set, in general, leads to bond contraction, the CCSD(T)/cc-pV5Z results compare less favourably with experiment. The mean of the absolute value of the deviation from experiment is $|\bar{\Delta}|_{\text{CCSD(T)/cc-pV5Z}} = 0.18$ pm and the maximum deviation is 0.4 pm (CH_2). Therefore, unless it is possible to obtain a reliable estimate of the correlation effects from quadruple and higher-order excitations, there appears to be little reason for carrying out calculations in basis sets beyond cc-pVQZ.

At the SCF and CCSD levels, the correlation errors are larger and balanced calculations would require smaller basis sets. Indeed, the levels SCF/cc-pVDZ and CCSD/cc-pVTZ seem to provide reasonable compromises between the errors in the one-electron treatment and in the N -electron treatment, at least for the calculation of molecular equilibrium structures of bonded systems. At the SCF/cc-pVDZ level, the mean absolute deviation from experiment is $|\bar{\Delta}|_{\text{SCF/cc-pVDZ}} = 2.15$ pm with a maximum deviation of 6.43 pm (F_2). Except for CH_2 , the calculated bond distances are shorter than experiment, why increasing the basis set further would result in an unbalanced description. At the CCSD/cc-pVTZ level, the mean absolute deviation from experiment is $|\bar{\Delta}|_{\text{CCSD/cc-pVTZ}} = 0.58$ pm, the maximum deviation is 1.96 pm (F_2), and all the bonds lengths are shorter than experiment. This accuracy is clearly intermediate between that of the SCF/cc-pVDZ and CCSD(cc-pVQZ) levels.

3.4. Bond angles

The H_2O and CH_2 equilibrium bond angles are listed in Table 4. For all basis sets, both bond angles decrease as we go from SCF to CCSD. In contrast, when triples are included at the CCSDT level, the two bond angles behave differently, decreasing in H_2O but increasing in CH_2 . We also note that these bond angles increase with the size of the basis set except when going from cc-pVTZ to cc-pVQZ in CH_2 , where the angle instead decreases.

Table 3
Comparison of theoretical and experimental equilibrium geometries. Bond lengths in pm and angles in degrees

Parameter	cc-pVQZ CCSDT result	Core correlation corrected result	Experiment
R_{HF}	91.516	91.585	91.680 ^a
R_{CO}	112.877	112.964	112.832 ^a
R_{NN}	109.746	109.786	109.768 ^a
R_{FF}	141.075	141.134	141.193 ^a
R_{HO}	95.620	95.688	95.72 ^b
\angle_{HOH}	104.25	104.21	104.52 ^b
R_{HC}	110.499	110.740	110.7 ^c
\angle_{HCH}	102.32	102.24	102.4 ^c

^a Ref. [12]. ^b Ref. [13]. ^c Ref. [14].

Table 4
Calculated bond angles in degrees in the H_2O and CH_2 molecules

	SCF	CCSD	CCSD(T)	CCSDT
H_2O				
cc-pVDZ	104.61	102.21	101.94	101.94
cc-pVTZ	106.00	104.04	103.73	103.74
cc-pVQZ	106.22	104.53	104.25	104.25
cc-pV5Z	106.33	104.80	104.54	
CH_2				
cc-pVDZ	102.74	100.58	100.59	100.72
cc-pVTZ	103.57	102.16	102.16	102.35
cc-pVQZ	103.72	102.12	102.12	102.32
cc-pV5Z	103.79	102.24	102.24	

A comparison of the CCSD(T) and CCSDT bond angles reveals different behaviors for the two molecules. For H_2O , the CCSD(T) and CCSDT bond angles agree to within 0.01° and both are smaller than the CCSD angle by about 0.3° . For CH_2 , in contrast, the CCSD and CCSD(T) bond angles agree to within 0.01° and the CCSDT angle is larger by about 0.2° . It appears the accurate description of bond angles is more difficult than the description of bond distances. Since we have calculated only two distinct bond distances in our study, this makes it considerably more difficult to establish trends and appropriate levels of theory for this particular property.

3.5. Core correlation

The calculations discussed so far have all been carried out in the correlation-consistent polarized valence basis sets cc-pVXZ with all electrons correlated. A proper correlation of all the electrons would seem to require the use of the core-valence cc-pCVXZ basis sets rather than the cc-pVXZ sets. In this section, we consider the correlation of the core electrons in more detail, basing our discussion on calculations carried out at the MP2 level, whose results are given in Table 5.

From Table 5, we observe that core-correlation leads to a decrease of the bond distances. The average contraction from MP2 (frozen core)/cc-pV5Z to MP2 (all electrons)/cc-pCV5Z is 0.18 pm, with a maximum contraction of 0.27 pm for CO and N_2 . Furthermore, this core-correlation contraction is overestimated in the cc-pVXZ basis sets — going

from MP2 (all electrons)/cc-pCV5Z to MP2 (all electrons)/cc-pV5Z, the average and maximum contractions are 0.10 and 0.24 pm (in CH_2), respectively.

Although the core-correlation effects are overestimated in the valence basis set, we note that the cc-pV5Z(all electrons) results are closer to the cc-pCV5Z(all electrons) results than are the cc-pV5Z(frozen core) results. The larger valence basis sets thus provide a reasonably accurate treatment of core-correlation effects. Apparently, as the valence basis sets become larger, the innermost basis functions extend into the outer core region, thereby providing some flexibility for a description of those core effects that are most important for bond formation.

For these systems, the effect of core correlation on the bond distances is rather small — significantly smaller than the basis set effects from cc-pVDZ to cc-pVTZ and the correlation effects from SCF to CCSD. Investigations of core-correlation effects should therefore only be undertaken in studies aiming for an accuracy higher than that provided at the CCSD/cc-pVTZ level — at least for molecules containing first-row atoms and hydrogen only.

Returning to our CCSDT (all electrons)/cc-pVQZ calculations, we first recall that, except for the CO bond distance, all the calculated bond distances are shorter than experiment. Since we have established that the valence sets overestimate the contraction of the bond distances due to core-correlation effects, we expect that an inclusion of core-correlating atomic orbitals should lead to an even better agreement with experiment. We have corrected our CCSDT (all electrons)/cc-pVQZ results for core correlation by

Table 5
Correlation effects on the equilibrium geometries at the quintuple zeta level of basis set at the MP2 level. Bond lengths in pm and angles in degrees

Parameter	cc-pV5Z frozen core	cc-pV5Z	cc-pCV5Z
R_{HF}	91.776	91.649	91.718
R_{CO}	113.411	113.054	113.141
R_{NN}	110.962	110.656	110.696
R_{FF}	139.595	139.369	139.428
R_{HO}	95.794	95.630	95.698
\angle_{HOH}	104.29	104.45	104.41
R_{HC}	110.206	109.770	110.011
\angle_{HCH}	102.21	102.43	102.35

adding to these the difference between the cc-pCV5Z and cc-pV5Z(all electrons) results obtained at the MP2 level (Table 5). The numbers obtained in this way are listed in column three of Table 3. Although not entirely rigorous, this correction gives an estimate of the equilibrium geometries that would be obtained with a correct treatment of the core-correlation effects, and we see that the agreement with experiment is improved. The mean of the absolute deviation from the experiment is now down to 0.06 pm with a maximum of 0.13 pm (CO), and for all the molecules except CO the agreement with experiment is better after the correction for core correlation has been added. Part of the small errors present at the CCSDT/cc-pVQZ level thus originates in an incomplete treatment of core-correlation effects.

4. Conclusions

Equilibrium geometries of CO, CH₂, F₂, HF, H₂O and N₂ have been calculated in the CCSDT model using the cc-pVDZ, cc-pVTZ and cc-pVQZ basis sets with all the electrons correlated. The results have been used to benchmark the accuracy of the SCF, CCSD and CCSD(T) models for the calculation of equilibrium geometries.

In general, we find that improvements in the correlation treatment from SCF to CCSD and from CCSD to either CCSDT or CCSD(T) always result in an increase of the bond length. Conversely, improvements in the one-electron treatment from cc-pVDZ to cc-pVTZ always result in a decrease of the bond length. Contractions are usually (but not always) observed when the basis set is increased beyond the cc-pVTZ level.

For bond lengths, the CCSD(T) model provides an excellent approximate treatment of the triple excitations. Beyond the cc-pVDZ level, the CCSD(T) bond lengths are always longer than the CCSDT bond lengths, but never by more than 0.06 pm. The quality of the CCSD(T) correction is independent of the overall magnitude of the correlation contribution. Furthermore, the difference between the CCSD(T) and CCSDT bond lengths is virtually the same in the cc-pVTZ and cc-pVQZ basis sets, making it possible to estimate reliably the CCSDT bond lengths in large basis sets from the corresponding CCSD(T) calcula-

tion if the difference between CCSDT and CCSD(T) is known at the cc-pVTZ level.

At the CCSDT/cc-pVQZ level, the discrepancy from the experimental bond lengths is only 0.11 pm on average. At the CCSD(T) level, an average change of 0.12 pm is observed between cc-pVQZ and cc-pV5Z, and we therefore expect our CCSDT/cc-pVQZ results to be within 0.3 pm from the basis set limit. The inclusion of core-correlating functions (i.e., going from cc-pVXZ to cc-pCVXZ) was shown to stretch the bonds by a few tenths of a pm, so the total discrepancy of 0.11 pm arises from cancellation of errors between correlation effects due to quadrupole and higher order excitations, basis set incompleteness errors, and incomplete treatment of core-correlation effects, all three of the order of a few tenths of a pm. Finally, due to the fact that increments in the level of correlation and basis set change the bond length in different directions, the sequence SCF/cc-pVDZ, CCSD/cc-pVTZ, CCSDT/cc-pVQZ (or CCSD(T)/cc-pVQZ) constitutes a hierarchy for calculations of bond lengths with a balanced treatment of correlation and basis set effects. A good improvement in the accuracy is observed at each level, and in general the convergence towards the experimental results are from below.

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