The accuracy of *ab initio* molecular geometries for systems containing second-row atoms

Sonia Coriani[a] and Domenico Marchesan
Dipartimento di Scienze Chimiche, Università degli Studi di Trieste, via Licio Giorgieri 1, I-34127 Trieste, Italy

Jürgen Gauss
Institut für Physikalische Chemie, Universität Mainz, D-55099 Mainz, Germany

Christof Hättig
Forschungszentrum Karlsruhe, Institute of Nanotechnology, P.O. Box 3640, D-76021 Karlsruhe, Germany

Trygve Helgaker
Department of Chemistry, University of Oslo, P. O. Box 1033 Blindern, N-0315 Oslo, Norway

Poul Jørgensen
Department of Chemistry, University of Århus, Langelandsgade 140, DK-8000 Århus C, Denmark

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The performance of the standard hierarchy of *ab initio* models—that is, Hartree–Fock theory, second-order Møller–Plesset theory, coupled-cluster singles-and-doubles theory, and coupled-cluster singles-doubles-approximate-triples theory—in combination with correlation-consistent basis sets is investigated for equilibrium geometries of molecules containing second-row elements. From an analysis on a collection of 31 molecules (yielding statistical samples of 41 bond distances and 13 bond angles), the statistical errors (mean deviation, mean absolute deviation, standard deviation, and maximum absolute deviation) are established at each level of theory. The importance of core correlation is examined by comparing calculations in the frozen-core approximation with calculations where all electrons are correlated. © *2005 American Institute of Physics*.
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I. INTRODUCTION

The prediction of molecular equilibrium structures is one of the most common tasks of computational chemistry. Indeed, equilibrium structures are usually accurately determined by standard electronic-structure models and often constitute a valid alternative to experimental measurements.[1] In particular, with the establishment of the standard hierarchies of basis sets (one-electron space) and wave-function models (*N*-electron space) over the last two decades, the accuracy of such calculations can now be systematically improved towards the exact solution—see, for example, the discussion in Ref. 2.

For molecules containing first-row atoms, the errors in the determination of equilibrium structures employing the standard series of *N*-electron models consisting of Hartree–Fock (HF) theory,[2,3] second-order Møller–Plesset (MP2) perturbation theory,[4–6] coupled-cluster singles-and-doubles (CCSD) theory,[7] and coupled-cluster singles-doubles-approximate-triples [CCSD(T)] theory[8,9] together with the correlation-consistent basis sets of Dunning and co-workers[10–18] are nowadays well established. Several statistical studies have been carried out on closed-shell molecules containing only hydrogen and first-row atoms, for which experimental data are well known. In a large basis-set study using cc-pVQZ sets, it was found that the mean (maximum) absolute bond-length errors are 2.6 (8.5), 0.5 (1.7), 0.7 (2.5), and 0.1 (0.6) pm for the HF, MP2, CCSD, and CCSD(T) models, respectively.[1,19–21]

For molecules containing second-row atoms, the intrinsic errors (i.e., the errors in the basis-set limit) are less well established, partly because of the more demanding computational requirements for such atoms (more electrons) and partly because the correlation-consistent (core-valence) basis sets only recently became available for these atoms.[16,17] Although many coupled-cluster equilibrium geometries obtained with these basis sets have been reported during the last three or four years (see, for example, Refs. 17 and 22–24), no statistical analysis of the performance of the different approaches has been carried out apart from Puzzarini's study on the *X*BS and *X*CP series (X=H,F,Cl).[22]

Taking advantage of the development of the DALTON (Ref. 25) and ACESII (Refs. 26 and 27) computer codes for the computation of CCSD(T) molecular gradients[28–30] and of the development of core-valence correlation-consistent basis sets for second- and third-row atoms,[17] we here analyze the performance of the standard *ab initio* models HF, MP2, CCSD, and CCSD(T) for the calculation of equilibrium structures of molecules containing one or more second-row atoms, paying special attention to the importance of core correlation.

[a]FAX: +390405583903. Electronic mail: coriani@units.it

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TABLE I. All-electron CCSD(T)/cc-pCVQZ and experimental equilibrium bond lengths (pm) for the chosen sample of molecules. Bonds are ordered according to increasing experimental length. The "bond labels" refer to the bond lengths included in the statistical sample.

Bond label	Molecule	Bond	Calculated	Experiment	Reference	Notes
1	ClOH	R_{OH}	96.3125	96.35(25)	49	
2	HCP	R_{CH}	107.0748	107.02(10)	50	
3	H_2CS	R_{CH}	108.5374	108.56(21)	51	
4	ClNO	R_{NO}	113.5837	113.357(25)	52	
5	OCS	R_{CO}	115.6183	115.617(14)	53	
6	HBS	R_{HB}	116.9857	116.98(4)	54	
7	HCl	R_{HCl}	127.3669	127.455	55	
8	FBS	R_{FB}	127.7466	127.62(2)	56	
9	H_2S	R_{HS}	133.5272	133.56	57	
10	PH_3	R_{PH}	141.1539	141.16(6)	58	
11	SO_3	R_{SO}	141.7940	141.75(20)	59	
12	SO_2	R_{SO}	143.1144	143.080(1)	60	143.078(3)[61]
13	S_2O	R_{SO}	145.5467	145.7(15)	62	
14	SiH_4	R_{SiH}	147.4221	147.418	63	
15	PN	R_{PN}	149.1431	149.0866	55	
16	SiO	R_{SiO}	151.1653	150.9739	55	
17	HSiCl	R_{SiH}	151.469	151.40	23	(R_e^{emp})[a]
18	SiH_2	R_{SiH}	151.2962	151.40	64	
19	CS	R_{CS}	153.6852	153.4941	55	
20	HCP	R_{CP}	154.0530	153.99(2)	50	
21	CS_2	R_{CS}	155.3302	155.259	65	
22	OCS	R_{CS}	156.2500	156.140(14)	53	
23	SiF_2	R_{SiF}	159.1931	159.01(1)	66	
24	HBS	R_{BS}	159.9445	159.78(1)	54	
25	ClBS	R_{BS}	160.615	160.49(1)	67	
26	FBS	R_{BS}	160.9913	160.91(2)	56	
27	H_2CS	R_{CS}	160.9677	161.10(8)	51	
28	ClF	R_{ClF}	162.8637	162.8313	55	
29	ClBS	R_{ClB}	168.205	168.06(1)	67	
30	ClOH	R_{ClO}	169.0152	169.08	49	
31	Cl_2O	R_{ClO}	169.6384	169.59(1)	68	
32	CCl_2	R_{ClC}	171.2504	171.13(10)	69	
33	BCl	R_{BCl}	171.6578	171.59	55	
34	BCl_3	R_{BCl}	173.6050	174.0(4)	70	
35	S_2O	R_{SS}	188.5254	188.7(12)	62	
36	P_2	R_{PP}	189.5158	189.34	55	
37	SiS	R_{SiS}	193.1867	192.9321	55	
38	ClNO	R_{ClN}	196.5775	197.453(25)	52	
39	Cl_2	R_{ClCl}	199.1397	198.79	55	
	Cl_2S	R_{ClS}	201.4176	201.28(11)	71	(R_s)[b]
40	Cl_2Si	R_{ClSi}	206.7952	206.5310(26)	72	
41	HSiCl	R_{ClSi}	207.122	207.24	23	(R_e^{emp})[a]

[a]"Empirical" parameter, obtained in Ref. 23 from a revision of the experimental equilibrium bond lengths by Harper and Clouthier (Ref. 3), $R_{SiCl}=206.7(3)$ pm; $R_{SiH}=152.5(5)$ pm, with vibration-rotation constants calculated at the CCSD(T)/cc-pCVTZ level. Suggested "best" equilibrium values are $R_{SiCl}=207.1(1)$ pm, $R_{SiH}=151.4(1)$ pm, see Ref. 23 for details.

[b]The given experimental bond length is an R_s value. This bond distance has been excluded from the statistical sample as no experimental equilibrium value is available.

II. COMPUTATIONAL DETAILS

We have considered a sample of 32 molecules, containing a total of 42 unique single, double, and triple bonds listed (in order of increasing bond length) in Table I and a total of 14 bond angles similarly listed in Table II. Because of the lack of literature data for the experimental equilibrium bond length and bond angle of Cl_2S, only 41 bond lengths and 13 bond angles were included in the statistical samples of bond lengths and bond angles, respectively. The results for Cl_2S are nonetheless kept in the tables for future reference.

The results have been analyzed in terms of the deviations $\Delta_i=R_i^{calc}-R_i^{exp}$, the mean deviation $\bar{\Delta}=(1/n)\Sigma_{i=1}^{n}\Delta_i$, the standard deviation $\Delta_{std}=\sqrt{[1/(n-1)]\Sigma_{i=1}^{n}(\Delta_i-\bar{\Delta})^2}$, the mean absolute deviation $\bar{\Delta}_{abs}=(1/n)\Sigma_{i=1}^{n}|\Delta_i|$, the maximum absolute deviation $\bar{\Delta}_{max}=\max_i|\Delta_i|$, and the normal distribution function

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TABLE II. All-electron CCSD(T)/cc-pCVQZ and experimental equilibrium bond angles (°) for the chosen sample of molecules. Angles are ordered according to increasing experimental angle. The "labels" refer to the bond angles which are included in the statistical sample.

Label	Molecule	Angle	Calculated	Experiment	Reference	Notes
1	SiH_2	∠(HSiH)	92.203	92.08	64	
2	H_2S	∠(HSH)	92.290	92.11	57	
3	PH_3	∠(HPH)	93.482	93.33(2)	58	
4	HSiCl	∠(HSiCl)	95.303	94.66	23	$(\theta_e^{emp})^a$
5	SiF_2	∠(FSiF)	100.911	100.76(2)	66	
6	Cl_2Si	∠(ClSiCl)	101.529	101.3240(16)	72	
7	HOCl	∠(ClOH)	102.770	102.45(42)	49	
	Cl_2S	∠(ClSCl)	102.706	102.71(09)	71	$(\theta_s)^b$
8	CCl_2	∠(ClCCl)	109.279	109.22(10)	69	
9	Cl_2O	∠(ClOCl)	110.982	110.88(1)	68	
10	ClNO	∠(ClNO)	113.339	113.320(13)	52	
11	H_2CS	∠(HCH)	116.294	116.30(25)	74	
12	S_2O	∠(SSO)	118.038	118.01(43)	62	
13	SO_2	∠(OSO)	119.485	119.329(2)	60	

[a]Empirical parameter, obtained in Ref. 23 from revision of the experimental equilibrium bond angle by Harper and Clouthier (Ref. 73), ∠(HSiCl)=96.9(5)°, by means of vibration-rotation constants calculated at the CCSD(T)/cc-pCVTZ level. Suggested best equilibrium value is ∠(HSiCl)=95.0(5)°, see Ref. 23 for details.
[b]The given experimental angle is a θ_s value. This bond angle has been excluded from the statistical sample, as no experimental equilibrium estimate is available.

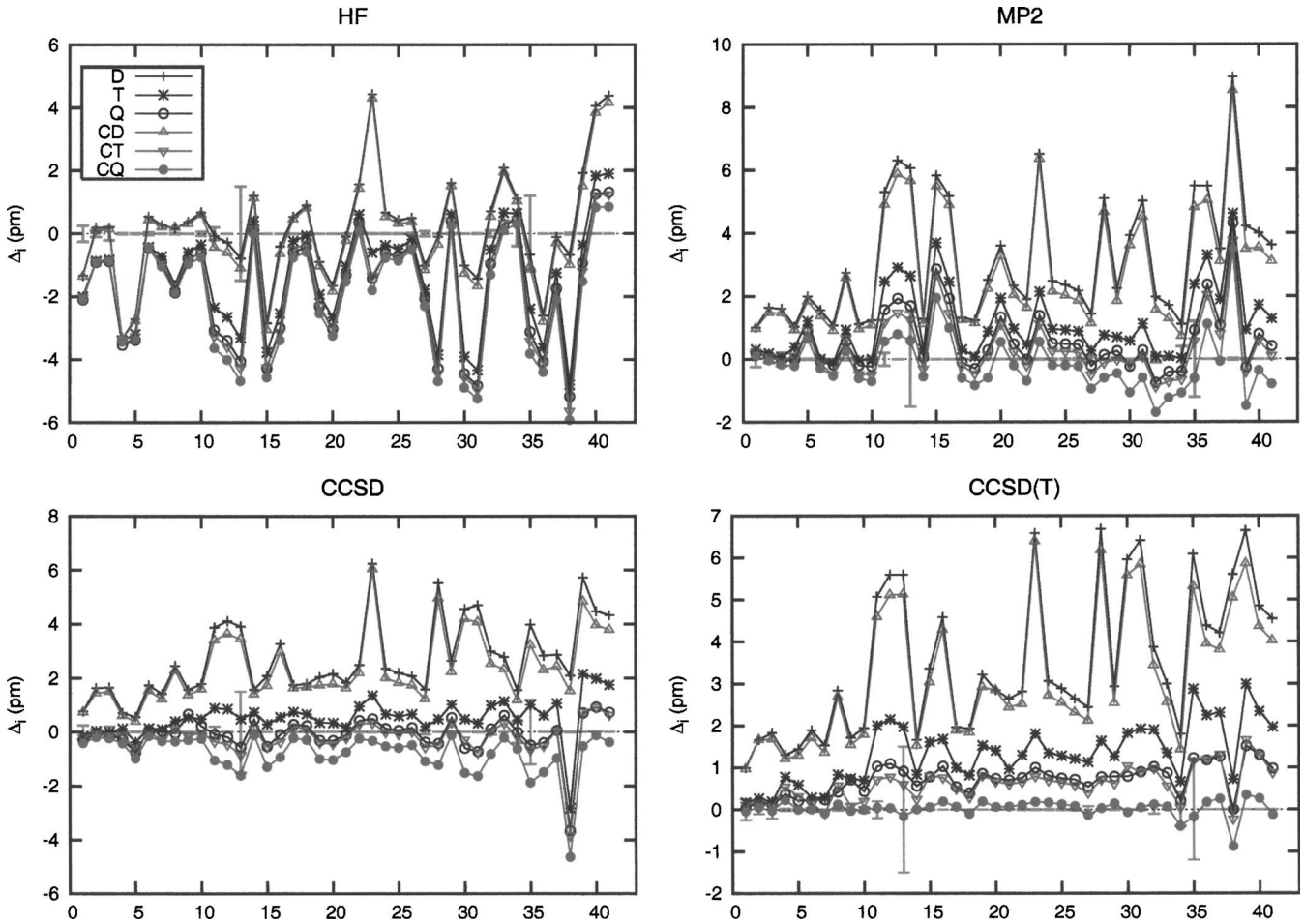


FIG. 1. Deviations Δ_i from experiment of the calculated equilibrium bond distances (pm) for the chosen sample of molecules in the valence cc-pV*X*Z (frozen core) and core-valence cc-pCV*X*Z (all electron) basis sets. The numbers in abscissa indicate the bond labels listed in Table I.

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TABLE III. Statistical measures of errors in calculated bond lengths (pm). For the correlated methods only the valence electrons were correlated in the valence basis sets.

		cc-pV*X*Z			cc-pCV*X*Z		
		D	T	Q	D	T	Q
HF	$\bar{\Delta}$	0.155	−1.377	−1.747	−0.003	−1.782	−2.012
	Δ_{std}	1.720	1.697	1.753	1.719	1.807	1.842
	$\bar{\Delta}_{\mathrm{abs}}$	1.234	1.701	1.950	1.266	1.983	2.130
	$\bar{\Delta}_{\mathrm{max}}$	4.053	4.798	5.176	3.839	5.638	5.915
MP2	$\bar{\Delta}$	3.149	1.136	0.582	2.840	0.367	−0.144
	Δ_{std}	1.984	1.154	1.016	1.898	0.950	0.936
	$\bar{\Delta}_{\mathrm{abs}}$	3.149	1.144	0.746	2.840	0.673	0.709
	$\bar{\Delta}_{\mathrm{max}}$	8.960	4.618	4.319	8.531	3.770	3.494
CCSD	$\bar{\Delta}$	2.698	0.545	−0.087	2.350	−0.204	−0.795
	Δ_{std}	1.394	0.755	0.710	1.275	0.704	0.787
	$\bar{\Delta}_{\mathrm{abs}}$	2.698	0.709	0.423	2.350	0.414	0.795
	$\bar{\Delta}_{\mathrm{max}}$	5.720	2.824	3.657	4.960	3.835	4.632
CCSD(T)	$\bar{\Delta}$	3.489	1.337	0.706	3.172	0.606	0.026
	Δ_{std}	1.745	0.722	0.371	1.599	0.408	0.200
	$\bar{\Delta}_{\mathrm{abs}}$	3.489	1.337	0.706	3.172	0.621	0.133
	$\bar{\Delta}_{\mathrm{max}}$	6.683	2.990	1.511	6.179	1.663	0.875

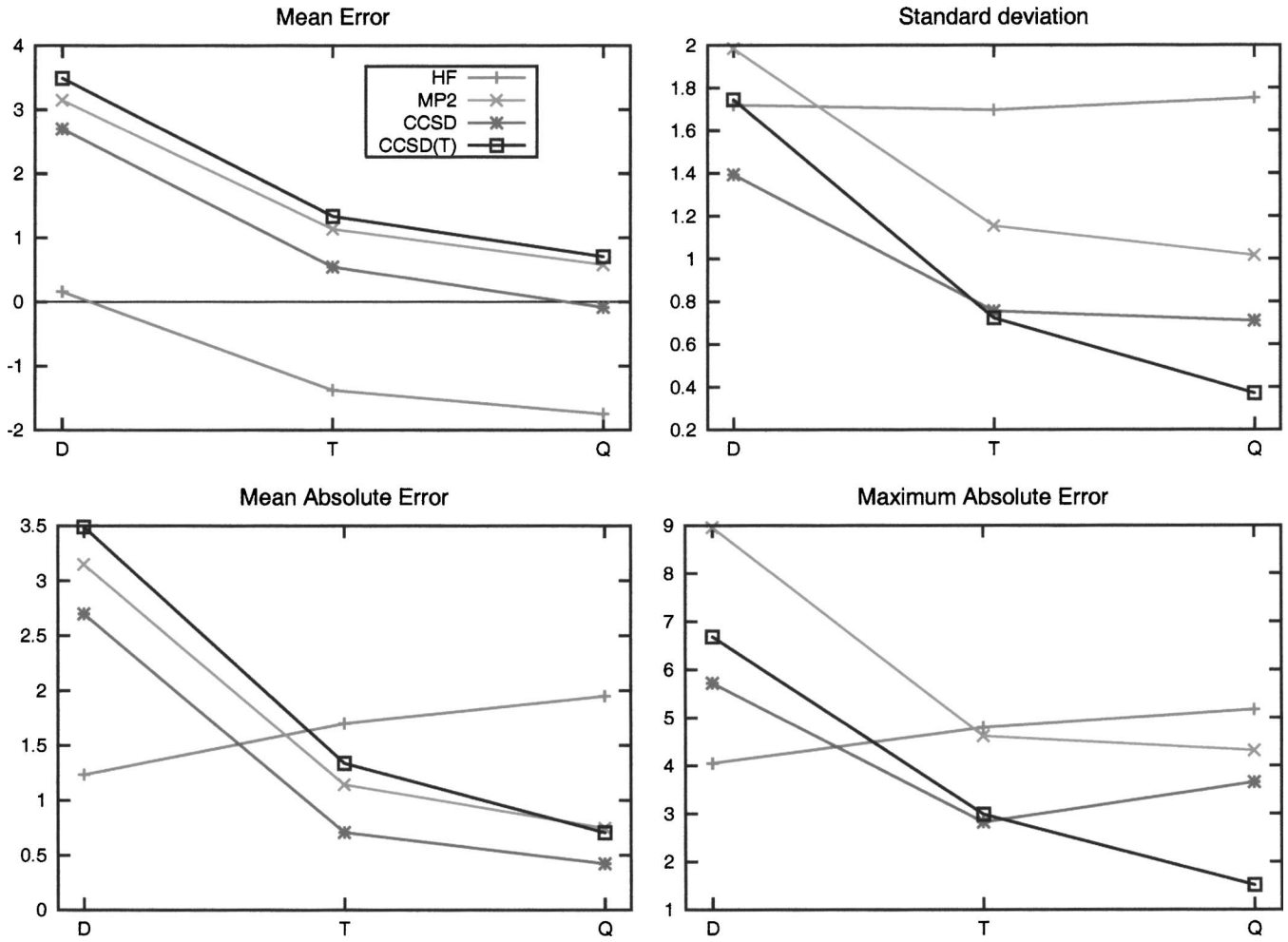


FIG. 2. Convergence trends of the statistical parameters for the bond distances (pm) in the valence cc-pV*X*Z sets (frozen core).

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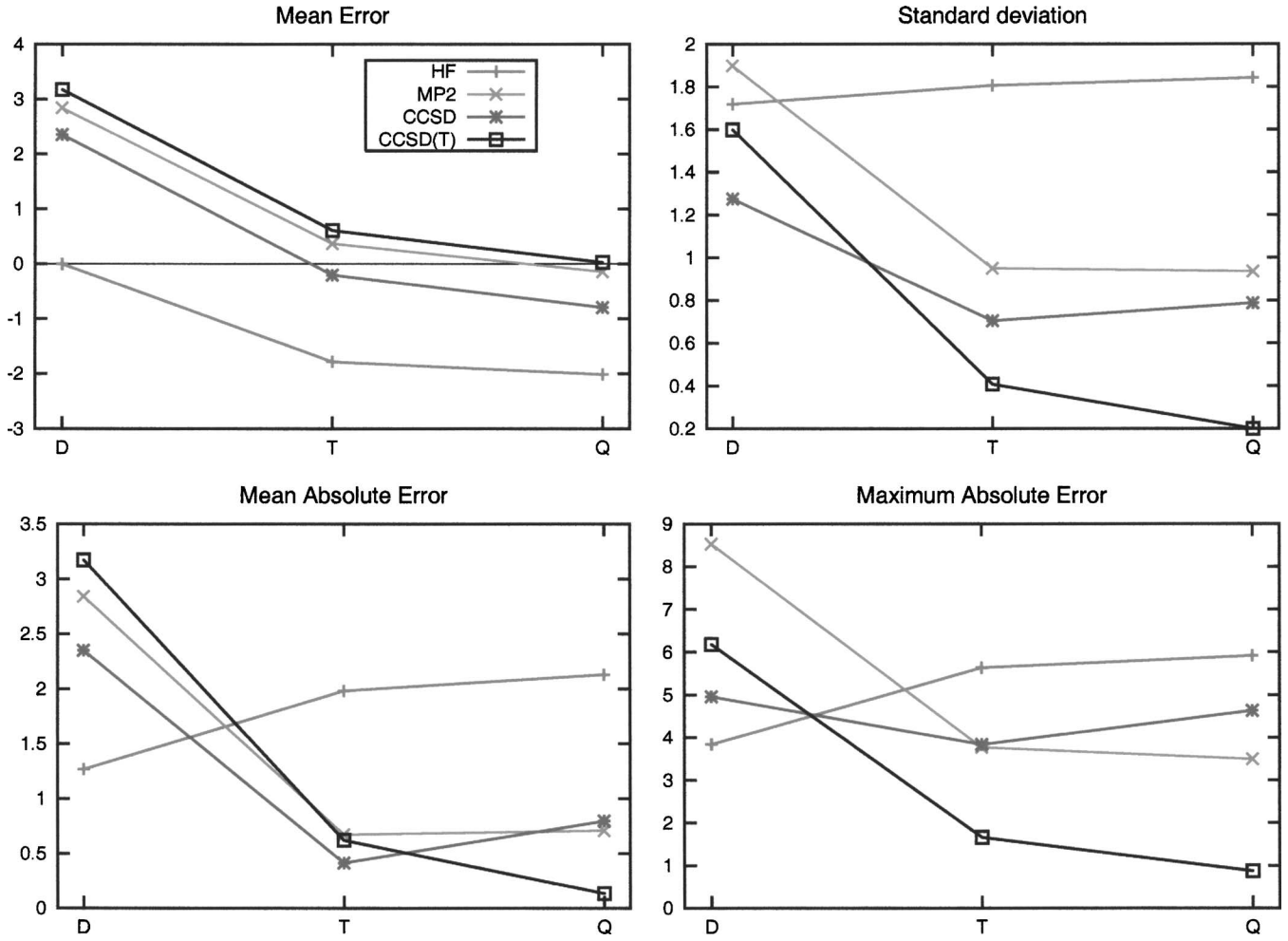


FIG. 3. Convergence trends of the statistical parameters for the bond distances (pm) in the core-valence cc-pCV*X*Z sets (all electron).

$$\rho(\Delta) = \frac{1}{\sqrt{2\pi}\Delta_{\text{std}}} \exp\left[-\frac{1}{2}\left(\frac{\Delta - \bar{\Delta}}{\Delta_{\text{std}}}\right)^2\right]. \quad (1)$$

Even though we cannot claim that the deviations follow a normal distribution, it is useful to represent the data in terms of such a function to obtain a visualization of the various levels of theory. Whereas the center of the distribution is related to systematic errors, its width reflects unsystematic errors characteristic of the approximation.

The calculations were performed with a development version of DALTON,[25] containing the gradient implementation of Ref. 28, and with ACESII,[26,27] using the gradient implementation described in Refs. 29 and 31. We used the the correlation-consistent polarized valence basis sets cc-pV*X*Z,[12,13] the standard polarized core-valence basis sets cc-pCV*X*Z, the weighted polarized core-valence basis sets cc-pwCV*X*Z (Refs. 17 and 18), and the revised polarized valence basis sets cc-pV(X+d)Z.[16] All sets were used with cardinal numbers $2 \leqslant X \leqslant 4$.

All calculations with valence basis sets were carried out in the frozen-core approximation, whereas the core-valence calculations were carried out with only the second-row 1*s* electrons frozen, as recommended in Ref. 17. The latter calculations are here referred to as "all electron."

III. DISCUSSION

Because of the large amount of data, we do not discuss all results in detail here but focus on the statistical measures, commenting in some cases on individual CCSD(T) results in the larger basis sets. For the entire set of data, see Ref. 32.

A. Individual errors

We begin our discussion with a brief analysis of the deviations from the experimental values of the bond distances as illustrated for all four methods and the six "standard" basis sets (cc-pV*X*Z and cc-pCV*X*Z) in Fig. 1. In the plots, the experimental error bars are also given when available.

The Hartree–Fock results show large deviations from experiment. In the small double-zeta basis sets, the deviations are positive as well as negative, leading to an overall relatively small mean deviation (*vide infra*). In larger sets, the bond distances become too short, falling well outside three standard deviations of the experimental values, the few exceptions ascribable to remarkably large experimental uncertainties.

In the correlated calculations, the smallest basis sets yield the largest errors, the bond distances shortening with improvements in the basis set. The MP2 deviations are

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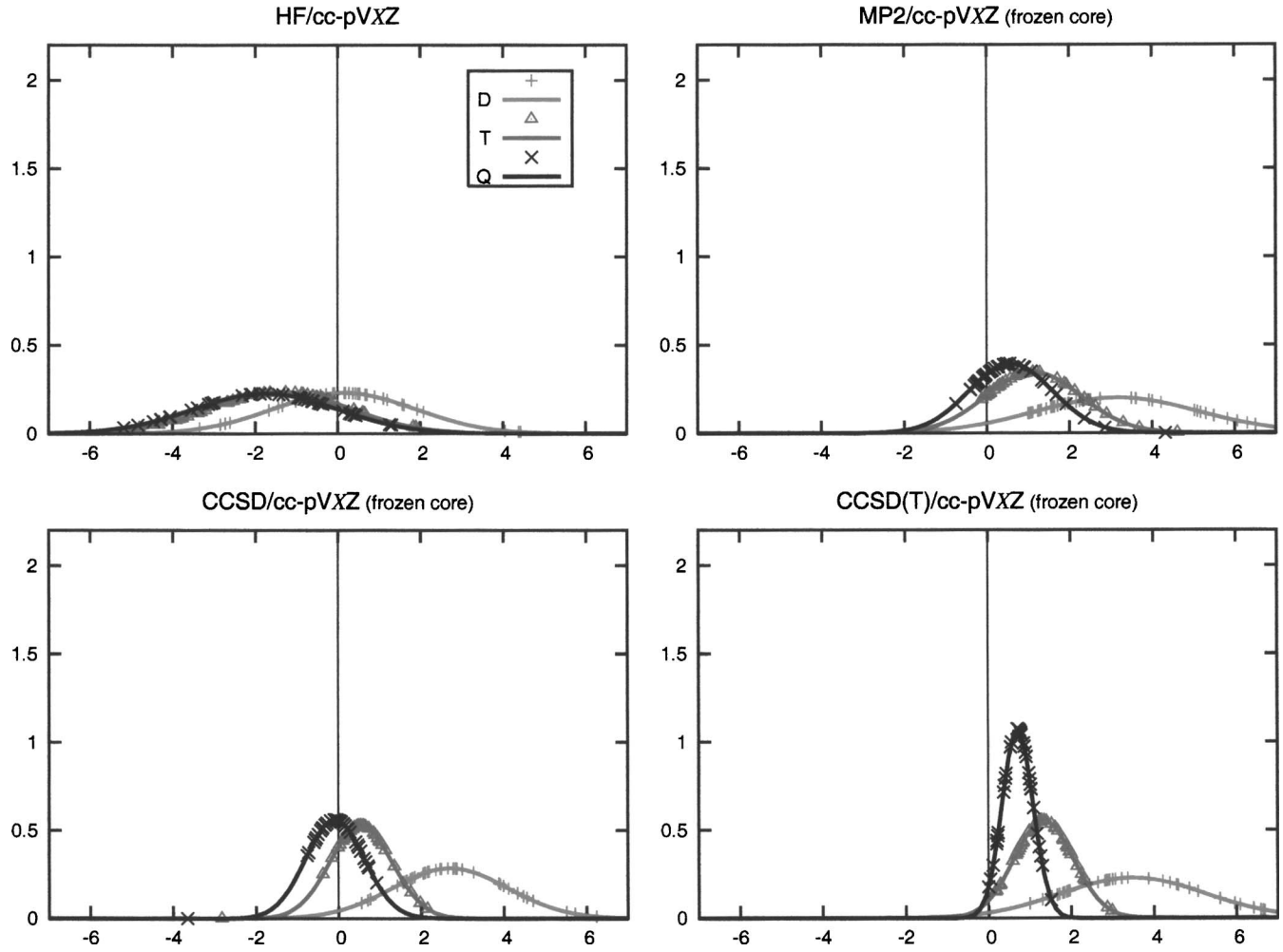


FIG. 4. Normal distribution functions $\rho(\Delta)$ of the deviations from experiment of the calculated bond distances (pm) in the valence cc-pV*X*Z sets (frozen core). The dots represent the values $\rho(\Delta_i)$ for the deviations Δ_i in the statistical sample.

mostly positive for $X \leqslant 3$, then become predominantly negative. At CCSD level, the errors are smallest in the cc-pVQZ and cc-pCVTZ basis sets, increasing (in absolute value) in the cc-pCVQZ basis. They are also mainly negative at $X=4$. It appears that the frozen-core CCSD/cc-pVQZ model is capable of yielding results in reasonable agreement with experiment. The CCSD/cc-pCVTZ level is unbalanced in the sense that large changes are observed as we go to the cc-pCVQZ basis, even though the agreement with experiment becomes poorer.

At the CCSD(T) level of theory, the systematic improvement with increasing cardinal number is evident, with essentially all cc-pCVQZ deviations being smaller than 0.3 pm. (Note the different ordinate scales in the plots of Fig. 1.) As seen from the figure, only three bond distances have errors larger than 0.3 pm—namely, BCl_3 (bond 34), Cl–N in ClNO (bond 38), and Cl_2 (bond 39). We shall return to this point later.

B. Statistical errors

In Table III, we have listed the mean deviations, the mean absolute deviations, the standard deviations, and the maximum absolute deviations for the valence-electron bond lengths calculated in the cc-pV*X*Z basis sets and for the all-electron bond lengths calculated in the cc-pCV*X*Z basis sets, respectively. The basis-set convergence patterns of these statistical measures are depicted in Figs. 2 and 3, respectively, for the valence- and all-electron calculations.

For all methods in Fig. 2, the bond lengths decrease with increasing cardinal number of the valence basis set cc-pV*X*Z, in the same manner as for molecules containing only first-row atoms.[2,19] In the small cc-pVDZ basis, the errors are smallest for the HF model, because of a cancellation between basis-set and correlation errors. But, whereas the HF results become less balanced with increasing cardinal number, the correlated models become more accurate, illustrating the need always to use basis sets larger than cc-pVDZ [and preferably of at least quadruple-zeta quality, in particular, at CCSD(T) level] in correlated calculations.

In the frozen-core calculations in Fig. 2, the statistical errors of the correlated models decrease with increasing cardinal number, except that $\bar{\Delta}_{\max}$ increases for the CCSD model when going from the triple- to quadruple-zeta basis set. It is noteworthy that, in the frozen-core calculations, the smallest mean and mean absolute errors are observed for the CCSD model rather than for the CCSD(T) model, at least for basis sets up to cc-pVQZ. Apparently, the error introduced by the neglect of triples in the CCSD model is to some extent

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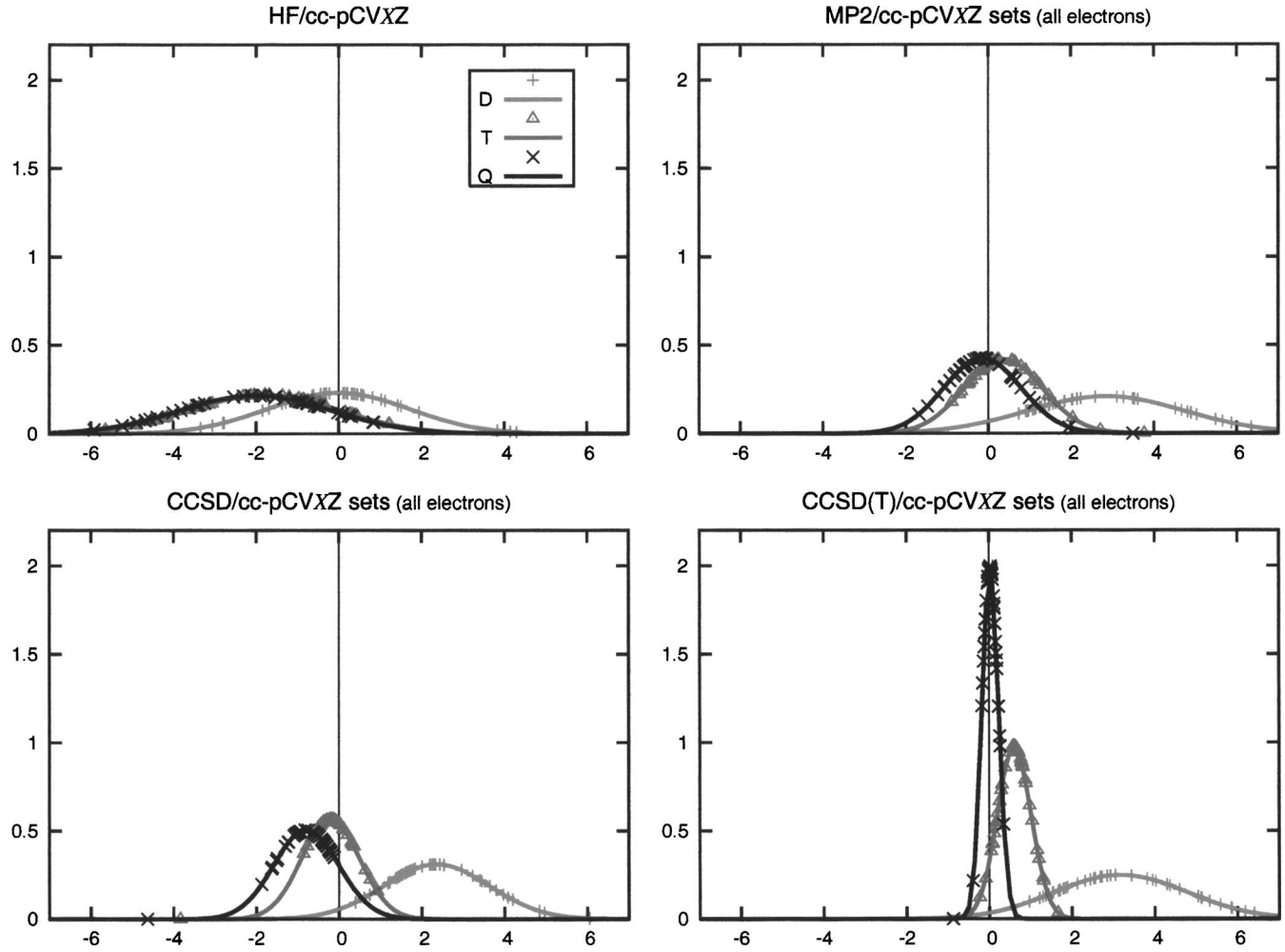


FIG. 5. Normal distribution functions $\rho(\Delta)$ of the deviations from experiment of the calculated bond distances (pm) in the core-valence cc-pCV*X*Z sets (all electron). The dots represent the values $\rho(\Delta_i)$ for the deviations Δ_i in the statistical sample.

canceled by the neglect of core correlation. Still, the performance of the CCSD(T) model is more systematic, with the smallest standard deviation and smallest maximum error in the cc-pVQZ basis.

For the all-electron calculations in Fig. 3, the situation is similar to that for the valence calculations in Fig. 2 except that the bonds are shorter, as seen by comparing the plots of the mean errors. As a result, the CCSD(T) model is now the most accurate one, at least for cardinal numbers $X \geqslant 4$. Clearly, there is little point in carrying out all-electron CCSD(T) calculations in a basis smaller than cc-pCVQZ. We note that the all-electron CCSD model underestimates bond lengths by about 1 pm in the basis-set limit, with a rather large standard deviation of 0.8 pm and a maximum error of 5 pm. For the all-electron CCSD(T) model, the standard deviation and maximum absolute error are only 0.2 and 1 pm, respectively.

TABLE IV. Valence-electron MP2 statistical measures of errors in the calculated bond lengths (pm). Comparison of results using either the cc-pV*X*Z or the cc-pV(X+d)Z set for the second-row atoms.

	$\bar{\Delta}$	Δ_{std}	$\bar{\Delta}_{\text{abs}}$	$\bar{\Delta}_{\text{max}}$
cc-pVDZ	3.172	1.985	3.172	9.151
cc-pV(D+d)Z	2.023	1.643	2.125	8.547
cc-pVTZ	1.135	1.158	1.143	4.808
cc-pV(T+d)Z	0.664	0.997	0.765	4.577
cc-pVQZ	0.564	1.030	0.742	4.510
cc-pV(Q+d)Z	0.285	1.008	0.668	4.357

C. Normal distributions

We turn now our attention to the normal-distribution functions, plotted in Figs. 4 and 5 for the valence and all-electron calculations, respectively. In these plots, the dots represent the values $\rho(\Delta_i)$ for the deviations Δ_i in the statistical sample.

The normal-distribution plots clearly illustrate how bond lengths shorten with increasing the cardinal number (the peaks move to the left) and lengthen with improvements in the N-electron representation, the final accuracy depending on a cancellation of one- and N-electron errors. As noted above, bond distances are typically underestimated at the HF level and often overestimated at the correlated levels (an exception here is CCSD, in particular, when used together with the core-valence sets and $X > 2$). The HF method is characterized by very broad distributions, which move off the center with increasing cardinal number. In the cc-pVDZ and cc-pCVDZ basis sets, bond lengths are equally often under-

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TABLE V. Comparison of frozen-core CCSD(T)/cc-pVQZ and cc-pV(Q+d)Z bond lengths, all-electron CCSD(T)/cc-pCVQZ and cc-pwCVQZ bond lengths, and experimental equilibrium bond lengths (pm) for a subset of 22 bonds in the chosen sample of molecules.

Label	Molecule	Bond	cc-pVQZ	cc-pV(Q+d)Z	cc-pCVQZ	cc-pwCVQZ	Experiment
I	HCP	R_{CH}	107.2180	107.2167	107.0748	107.07[a]	107.02(10)[b]
II	OCS	R_{CO}	115.8270	115.8430	115.6183	115.5986	115.617(14)[c]
III	HBS	R_{HB}	117.2069	117.2113	116.9857	116.97[a]	116.98(4)[d]
IV	HCl	R_{HCl}	127.6926	127.5602	127.3669	127.3421	127.455[e]
V	FBS	R_{FB}	128.0376	128.0448	127.7466	127.70[a]	127.62(2)[f]
VI	PN	R_{PN}	149.8680	149.6295	149.1431	149.0271	149.0866[e]
VII	SiO	R_{SiO}	152.0055	151.7041	151.1653	150.9617	150.9739[e]
VIII	HSiCl	R_{HSi}	151.938	151.7962	151.469	151.4003	151.40[g]
IX	CS	R_{CS}	154.3483	154.1527	153.6852	153.6083	153.4941[e]
X	HCP	R_{CP}	154.7278	154.5467	154.0530	153.97[a]	153.99(2)[b]
XI	OCS	R_{CS}	156.8986	156.6851	156.2500	156.1823	156.140(14)[c]
XII	SiF_2	R_{SiF}	160.0077	159.6874	159.1931	159.0208	159.01(1)[h]
XIII	HBS	R_{BS}	160.5829	160.4561	159.9445	159.88[a]	159.78(1)[d]
XIV	ClBS	R_{BS}	161.236	161.1173	160.615	160.54	160.49(1)[i]
XV	FBS	R_{BS}	161.6221	161.4879	160.9913	160.92[a]	160.91(2)[f]
XVI	ClF	R_{ClF}	163.6086	163.1823	162.8637	162.8194	162.8313[e]
XVII	ClBS	R_{ClB}	168.843	168.6855	168.205	168.16[a]	168.06(1)[i]
XVIII	BCl	R_{BCl}	172.4609	172.3078	171.6578	171.5827	171.59[e]
XIX	P_2	R_{PP}	190.5176	190.1931	189.5158	189.4113	189.34[e]
XX	SiS	R_{SiS}	194.1928	193.8663	193.1867	193.0563	192.9321[e]
XXI	Cl_2	R_{ClCl}	200.3013	199.6573	199.1397	199.0584	198.79[e]
XXII	HSiCl	R_{ClSi}	208.216	207.7836	207.122	207.0036	207.24[g]

[a]From Ref. 22.
[b]From Ref. 50.
[c]From Ref. 53.
[d]From Ref. 54.
[e]From Ref. 55.
[f]From Ref. 56.
[g]From Ref. 23.
[h]From Ref. 66.
[i]From Ref. 67.

estimated and overestimated by HF theory; in larger basis sets, they are mostly but not invariably underestimated. Basis-set convergence is already reached in the cc-pVTZ basis, although some changes are observed when the cardinal number is incremented further and when core functions are added.

For the correlated models, our first observation is that the double-zeta basis sets (even with core functions included) are too small, producing bonds that are always too long. A considerable improvement is observed at the triple-zeta level, although a quadruple-zeta basis is needed in CCSD(T) theory for convergence. In passing, we note that the quadruple-zeta basis set is not needed for the connected triple excitations as such but rather for the doubles, which in CCSD(T) theory need to be more accurately described than in CCSD theory in order for the small triples correction to be truely useful.[33]

TABLE VI. CCSD(T) statistical measures of errors in the calculated bond lengths (pm). Comparison of results obtained using the cc-pVQZ, cc-pV(Q+d)Z, cc-pCVQZ, and cc-pwCVQZ basis sets for a subset of 22 bonds.

	Valence only		All electron	
	cc-pVQZ	cc-pV(Q+d)Z	cc-pCVQZ	cc-pwCVQZ
$\bar{\Delta}$	0.755	0.548	0.102	0.024
Δ_{std}	0.347	0.225	0.106	0.097
$\bar{\Delta}_{abs}$	0.755	0.548	0.121	0.069
$\bar{\Delta}_{max}$	1.511	0.934	0.350	0.268

Comparing the CCSD and MP2 models (both of which ignore connected triples), we first note that the MP2 model gives longer bonds than does the CCSD model. This behavior, which occurs also for molecules consisting only of first-row atoms, is typical of second-order perturbation theory,[1,19–21] as well as of the perturbative corrections used in CCSD(T). It is likewise observed, in fact, for CCSD(T) bond distances relative to CCSDT distances.[34,35] We next note that the normal distributions are slightly more central and peaked in valence-electron CCSD theory than in valence-electron MP2 theory. However, with core correlation included, the MP2 model typically gives a slightly better geometry, the all-electron CCSD/cc-pCVQZ bonds being too short. The better description of the electrons provided by the CCSD model is mainly reflected in its standard deviation, which is smaller than in MP2 theory. Also, the CCSD model is more robust than the MP2 model in the sense that it gives fewer outliers.

The CCSD(T) method shows an overall systematic be-

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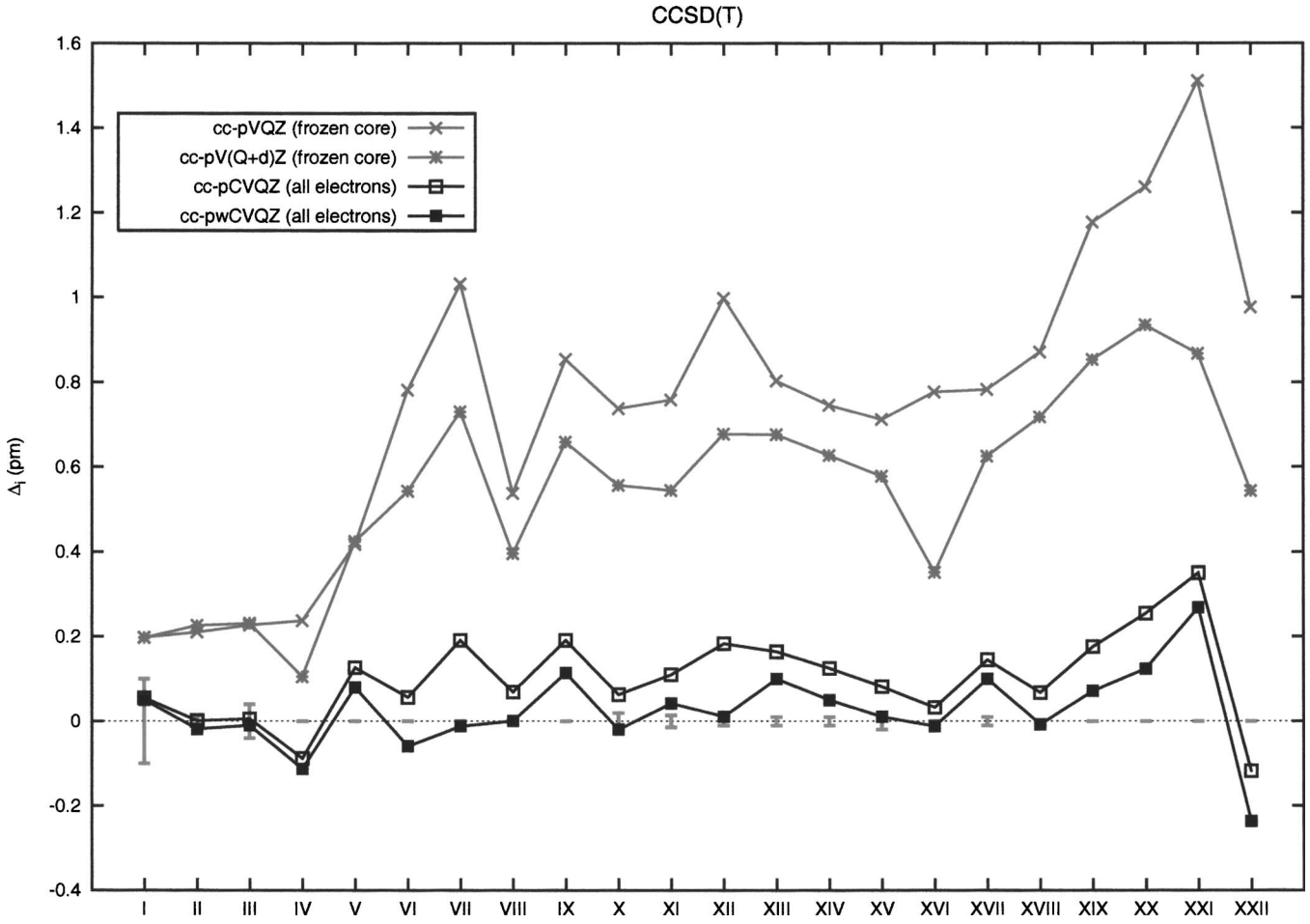


FIG. 6. Comparison of the deviations from experiment in the equilibrium bond distances (pm) for a subset of 22 bonds at the valence-electron CCSD(T) level in the cc-pVQZ and cc-pV(Q+d) basis sets, and at the all-electron CCSD(T) level in the cc-pCVQZ and cc-pwCVQZ basis sets. The roman numbers in abscissa indicate the bonds listed in Table V.

TABLE VII. Statistical measures of errors in calculated bond angles (°). For the correlated methods only the valence electrons were correlated in the valence basis sets.

		cc-pV*X*Z			cc-pCV*X*Z		
		D	T	Q	D	T	Q
HF	$\bar{\Delta}$	0.330	0.722	0.877	0.397	0.894	0.993
	Δ_{std}	1.466	1.432	1.442	1.428	1.344	1.389
	$\bar{\Delta}_{\mathrm{abs}}$	1.300	1.293	1.313	1.278	1.231	1.279
	$\bar{\Delta}_{\mathrm{max}}$	2.246	3.085	3.453	2.305	3.085	3.598
MP2	$\bar{\Delta}$	−0.183	−0.031	0.034	−0.138	0.117	0.137
	Δ_{std}	0.644	0.343	0.274	0.607	0.312	0.278
	$\bar{\Delta}_{\mathrm{abs}}$	0.513	0.252	0.188	0.466	0.281	0.250
	$\bar{\Delta}_{\mathrm{max}}$	1.724	0.630	0.666	1.680	0.521	0.555
CCSD	$\bar{\Delta}$	−0.277	0.066	0.159	−0.214	0.237	0.292
	Δ_{std}	0.687	0.434	0.419	0.635	0.312	0.377
	$\bar{\Delta}_{\mathrm{abs}}$	0.584	0.375	0.373	0.551	0.318	0.366
	$\bar{\Delta}_{\mathrm{max}}$	1.239	0.756	0.816	1.164	0.808	1.111
CCSD(T)	$\bar{\Delta}$	−0.323	−0.026	0.041	−0.264	0.139	0.164
	Δ_{std}	0.741	0.404	0.270	0.695	0.278	0.169
	$\bar{\Delta}_{\mathrm{abs}}$	0.554	0.296	0.198	0.510	0.224	0.165
	$\bar{\Delta}_{\mathrm{max}}$	1.880	0.730	0.607	1.806	0.788	0.643

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havior, the distributions becoming narrower and more central with each increment in the cardinal number—in particular, when core correlation is included, see Fig. 5. It is important to note, however, that high accuracy is only achieved with large basis sets and with all electrons correlated. Thus, at the double-zeta level, bond lengths are in some cases overestimated by more than 6 pm; in the cc-pCVQZ basis and with all electrons correlated, the largest deviation from experiment is 0.9 pm, the mean absolute error and standard deviation being 0.13 and 0.20 pm, respectively—see Table III.

It should be noted, however, that the all-electron CCSD(T)/cc-pCVQZ statistics are strongly affected by the inclusion in the sample of ClNO and BCl_3, for which the deviations are larger than 0.3 pm. If these molecules are excluded, the mean absolute error and standard deviation are reduced to 0.10 and 0.12 pm, respectively—see also the comparison of the cc-pCVQZ and cc-pwCVQZ in Sec. III D.

Thus, the high accuracy of the all-electron CCSD(T) model in a core-valence quadruple-zeta basis, already observed for molecules containing only first-row atoms, is also observed for molecules containing second-row atoms. In spite of the fact that the cc-pCVQZ does not represent the basis-set limit for the CCSD(T) model and in spite of the fact that the CCSD(T) model is not equal to the full configuration-interaction (FCI) model (noting that quadruple excitations have been found to be important in other instances[36,37]), it does represent a cost-effective way to calculate bond distances with an accuracy comparable to experiment.

D. The revised valence and weighted core-valence basis sets

We conclude our discussion of bond lengths by comparing the performance of the revised cc-pV(X+d)Z basis sets (designed for improved convergence of dissociation energies for molecules with second-row atoms) and the standard valence cc-pVXZ basis sets, and by comparing the performance of the weighted core-valence cc-pwCVQZ basis sets and the standard cc-pCVQZ basis sets.

In Table IV, we have collected the statistical parameters obtained at the valence-electron MP2 level of theory, using either the cc-pVXZ basis for all atoms or the cc-pV(X+d)Z basis for the second-row atoms and the cc-pVXZ basis for the remaining atoms. The reductions in the mean and maximum absolute deviations are small, at least at the quadruple-zeta level of theory: 0.67 and 4.4 pm, respectively, in the cc-pV(Q+d)Z basis versus 0.74 and 4.5 pm in the cc-pVQZ set. By contrast, a larger change is observed in the mean deviation, which is reduced from 0.56 pm in the standard basis to 0.29 pm in the revised basis. As expected, mainly bond distances involving second-row atoms are appreciably affected by the use of the revised basis sets, the effect on the other bonds being marginal (in particular on those between H and first-row atoms).

In Table V, we compare the results obtained at the valence-electron CCSD(T) level using either the cc-pVQZ basis or the cc-pV(Q+d)Z basis for the second-row atoms, for a subset of the considered molecules containing 22 bonds. For almost all bonds, and in particular those to second-row atoms, a small but significant shortening is observed when the cc-pV(Q+d)Z basis is used, improving the agreement with experiment. The effect on the statistical parameters is summarized in Table VI. Although we therefore advocate the use of the revised basis sets for second-row atoms, it should be recognized that, for a significant and systematic improvement relative to experiment, it is necessary to correlate the core electrons.

In Table V we also compare the all-electron CCSD(T) bond lengths obtained in the cc-pCVQZ and cc-pwCVQZ basis sets with experiment. The corresponding relative deviations from the experimental values are shown in Fig. 6, together with those for the standard and revised valence sets. In general, the deviations from experiment are smaller for the cc-pwCVQZ basis sets than for the cc-pCVQZ set. The statistical parameters, recalculated for these bonds, are also collected in Table VI. A slight improvement is observed for all statistical measures: $\bar{\Delta}$(cc-pCVQZ)=0.10 pm vs $\bar{\Delta}$(cc-pwCVQZ)=0.02 pm; Δ_{std}(cc-pCVQZ)=0.106 vs Δ_{std}(cc-pwCVQZ)=0.097; $\bar{\Delta}_{\mathrm{abs}}$(cc-pCVQZ)=0.12 pm vs $\bar{\Delta}_{\mathrm{abs}}$(cc-pwCVQZ)=0.07 pm and $\bar{\Delta}_{\mathrm{max}}$(cc-pCVQZ)=0.35 pm vs $\bar{\Delta}_{\mathrm{max}}$(cc-pwCVQZ)=0.27 pm. From Fig. 6, we note that the improvement with the weighted basis arises from a shortening of bond lengths. However, this improvement is marginal compared with the improvement observed by going from the cc-pCVTZ basis to the cc-pCVQZ basis. Still, since the cc-pwCVQZ and cc-pCVQZ basis sets are of the same size, we recommend the use of the weighted basis sets.

E. Statistics on bond angles

In Table II, we have listed the experimental bond angles for the molecules in Table I, along with the CCSD(T)/cc-pCVQZ bond angles. In Table VII the statistical errors for the standard levels of theory are collected, in the same manner as those for the bond lengths in Table III. Note that, whereas our bond-length analysis is based on a rather large sample of 41 bond lengths, the bond-angle sample contains 13 bond angles—a rather small sample, especially in view of the relatively large uncertainties in some of the experimental angles.

The errors in the bond angles follow the same pattern as for the bond lengths, which again are similar to those found for molecules containing only hydrogen and first-row atoms.[2,20] In general, bond angles increase with increasing cardinal number, so as to offset the increased repulsion between the two nonbonded atoms that follows from the simultaneous bond-length contraction.[2] From Tables II and VII, it appears that bond angles are relatively easily calculated to within a few tenths of a degree.

Comparing Tables III and VII, we note that the differences among the correlated models appear to be smaller for bond angles than for bond lengths. In the same manner, the differences between valence- and all-electron errors are smaller for bond angles than for bond lengths. However, these differences may not be intrinsic to the computational models but may follow from larger errors in the experimental

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bond angles than in the experimental bond distances (as reflected in the larger error bars for the bond angles).

IV. CONCLUSIONS

For molecules containing second-row atoms, we have examined the errors in bond distances and bond angles calculated with the standard *N*-electron models HF, MP2, CCSD, and CCSD(T) using correlation-consistent basis sets with cardinal numbers $X \leqslant 4$, with and without core correlation included. At the all-electron CCSD(T)/cc-pCVQZ level of theory, the mean absolute errors are 0.13 pm for bond lengths and 0.2° for bond angles; without core correlation, the CCSD(T)/cc-pVQZ errors are 0.7 pm and 0.2°, respectively. Without core correlation, the errors in the equilibrium structures are thus almost 1 pm. The errors are slightly reduced by using the cc-pwCVQZ basis rather than the cc-pCVQZ basis. At the all-electron CCSD/cc-pCVQZ level of theory, the mean absolute errors are 0.8 pm and 0.4°, respectively, while the corresponding MP2 errors of 0.7 pm and 0.3° are slightly smaller—that is, about an order or magnitude larger than at the CCSD(T) level of theory.

To reduce errors below 0.1 pm, we must improve the one-electron description by going beyond the quadruple-zeta level or by using basis-set extrapolation,[38,39] and we must also improve the *N*-electron description by relaxing the triples[34,40] and by including higher excitations. For molecules consisting of first-row atoms, basis-set extension beyond $X=4$ shortens bonds by about 0.1 pm, triples relaxation shortens them further by a smaller amount, whereas the inclusion of quadruples lengthen the bonds by 0.1–0.2 pm,[36,37,41–44] leading to a well balancing of the errors in calculations at the CCSD(T)/cc-pCVQZ level. A similar cancellation of errors may be expected for molecules containing also second-row atoms judging from the results of this investigation.

Another aspect that warrants further attention is the accuracy of the experimental data. The experimental data used in this investigation are of variable accuracy, depending on the system complexity. The statistical analysis depends critically on this accuracy, as demonstrated, for instance, by the reduction of the CCSD(T)/cc-pCVQZ mean absolute error to 0.1 pm if the data for ClNO and BCl_3 are not taken into account. Even though it could be argued that the large deviations between calculated and experimental results for ClNO depend on an incomplete treatment of electron correlation,[45,46] it may in general be appropriate to revise the experimental data. Empirical equilibrium geometries, based on experimental rotational constants and calculated vibration-rotation interaction constants,[21,47,48] offer an attractive route to more accurate reference data. Such a revision, previously undertaken for molecules containing first-row atoms,[21] is planned for molecules containing second-row atoms.

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