14530 *J. Phys. Chem. A* **2009,** *113,* 14530–14535

Extrapolation to the Complete Basis Set Limit of Structural Parameters: Comparison of Different Approaches[†]

Cristina Puzzarini[‡]

Dipartimento di Chimica "G. Ciamician", Università degli Studi di Bologna, Via Selmi 2, I-40126 Bologna, Italy

Received: April 30, 2009; Revised Manuscript Received: August 26, 2009

For the first time, different procedures for extrapolating structural parameters to the complete basis set limit are compared. More precisely, a well-tested scheme, based on extrapolated gradients, is employed for validating the extrapolation procedure directly applied to geometrical parameters by means of different extrapolation functions. For this purpose, a set of small systems (mostly triatomics), also containing second-row elements, has been chosen.

Introduction

Achievement of the complete basis set (CBS) limit in equilibrium geometry calculations is an important step toward the quantitative accuracy for theoretical predictions. Taking a step back, the accuracy in molecular structure computations depends on the electron-correlation treatment chosen and the basis set employed. Concerning the former, the coupled-cluster theory, and in particular the CCSD(T) method,[1] has turned out to be the standard approach. In fact, it is well-established that this level of theory in conjunction with a sufficiently large one-particle basis set is able to provide an accuracy of 0.002−0.003 Å for bond distances.[2−4] With respect to the basis set issue, it is worth mentioning that the convergence to the CBS limit is rather slow for correlated methods,[5] which means that calculations employing a basis set as large as Dunning's cc-pV6Z basis[6,7] do not provide the CBS limit.

Focusing on the extrapolation to the CBS limit issue, it has to be noted that, while theoretically based and/or well-tested approaches are available for energies (see for instance refs 5 and 8−15), little has been done for properties. To our knowledge, the best available scheme for molecular structure is that proposed by Gauss and co-workers,[16] which is based on the additivity scheme of ref 17 and the extrapolation is performed at the energy gradient level ("gradient scheme"). As evident from ref 16, this procedure has been validated by means of CCSD(T)-R12 calculations[13,15,18,19] which are CCSD(T) computations for which the convergence to the CBS limit is significantly accelerated because of the explicit inclusion of the interelectronic distance in the wave function ansatz.

On an empirical basis, the extrapolation to the CBS limit can also be directly applied to geometrical parameters ("geometry scheme"). On this topic, even if a comprehensive review of the CBS extrapolation literature is beyond the scope of the present work, the pioneering work of Feller (see for instance refs 20 and 21), Dunning and Peterson (see for example refs 22 and 23) and Martin and Taylor (see for example refs 24 and 25) has to be cited. Despite application of the "geometry scheme" to different systems, either closed-shell or open-shell, either neutral or ionic species (see for instance refs 26−32), a systematic investigation aiming at its validation is still missing. For this reason, in the present study results from this extrapolation scheme, also employing different functions, are compared to those obtained from the "gradient scheme" for a set of molecules, mostly triatomic systems. Triatomics have been chosen because they easily allow the comparison with another extrapolation procedure, which is actually equivalent to the "gradient scheme", and that we refer to as the "energy scheme". In fact, for these species the near-equilibrium potential energy surface (PES) can be constructed and, by extrapolating the energy point by point, its CBS limit can be derived. Even if theoretically equivalent to the "gradient scheme", this approach has been employed with the aim of performing numerical consistency checks. Unlike the other procedures, the main advantage of the "geometry scheme" is that it is always applicable and is definitely less computationally expensive than the "gradient scheme".

Even if a limited number of systems has been considered, we have tried to make the set as significant as possible. In particular, species containing second-row elements, for which the convergence to the CBS limit is known to be slower, have been considered. Going into detail the molecules investigated are

(1) Neutral closed-shell species containing only first-row elements (HCN, HNC, FCN, H_2O, CO_2, NH_3) as well as containing second-row atoms (XSiY, with X = F, Cl and Y = N, P; XCP, with X = H, F, and PH_3).

(2) Neutral open-shell species (HCS, HSC, NH_2, and PH_2) and cationic closed-shell species (HCS^+ and HSC^+).

In the following section the methodology will be described and all computational details will be provided. Thereafter, the results will be reported and discussed.

Methodology

The CFOUR program package[33] as well as the MOLPRO suite of programs[34] have been employed in the present study. All calculations have been performed at the CC singles and doubles (CCSD) level augmented by a perturbative treatment of triple excitations (CCSD(T))[1] in conjunction with correlation consistent basis sets. More precisely, the cc-pVnZ hierarchical sequence of bases sets,[6,7] with n = T, Q, 5, 6, have been employed. The frozen core approximation has always been adopted; i.e., only valence electrons have been correlated. Test computations, carried out at the multiconfiguration self-consistent field (MCSCF)[35,36] as well as coupled cluster levels of theory in conjunction with a basis of triple-ζ quality, showed

---

[†] Part of the "Vincenzo Aquilanti Festschrift".

[‡] E-mail: cristina.puzzarini@unibo.it.

10.1021/jp9040327

that in all cases the electronic ground state is well described by a single reference wave function. T_1[37,38] and D_1[39] diagnostics also supported such conclusion.

As mentioned in the Introduction, different approaches have been employed for obtaining the CBS limit of structural parameters. The first one, named as "geometry scheme", requires geometry optimizations to be carried out at the CCSD(T)/cc-pVnZ level, with n = T, Q, 5, and 6. To this purpose, the MOLPRO program,[34] and consequently numerical gradients,[40,41] have been used.[42] As convergence criteria, the maximum component of the gradient as well as the maximum component of the step have been constrained to be lower than 1.0×10^{-6} au. Then, the systematic trend of geometrical parameters has been exploited to estimate the CBS limit by making use of the assumption that the convergence of the structural parameters has the same behavior as energy. To this end, different formulas have been employed, but it has to be stressed once more that in all cases they are empirical and lack any theoretical justification. First of all, the convergence for the correlation contribution has been described by the consolidated n^{-3} extrapolation formula:[10]

$$\Delta r^{\mathrm{corr}}(n) = \Delta r^{\mathrm{corr}}_{\infty} + An^{-3} \tag{1}$$

and it is applied to the case n = 5 and 6 (but also n = Q and 5; see next section). To obtain the extrapolated structure, the CBS limit value of the correlation contribution has then been added to the HF-SCF CBS limit, which is assumed to be reached at the HF-SCF/cc-pV6Z level:

$$r(\mathrm{CBS}) = r^{\mathrm{SCF}}_{\infty} + \Delta r^{\mathrm{corr}}_{\infty} \tag{2}$$

In addition to this procedure, three other extrapolation formula have also been considered: a mixed exponential/Gaussian function of the form[43,44]

$$r(n) = r_{\infty} + B\mathrm{e}^{-(n-1)} + C\mathrm{e}^{-(\mathrm{n}-1)^2} \tag{3}$$

a simple ("pure") exponential function[20,21]

$$r(n) = r_{\infty} + B'\mathrm{e}^{-C'n} \tag{4}$$

and the function of eq 1[10] applied to the whole parameter

$$r(n) = r_{\infty} + A'n^{-3} \tag{5}$$

without a distinction between SCF and correlation contributions, which is formally not correct but of quite common use.

To test the validity of the so-called "geometry scheme", i.e., to check the reliability of the extrapolation to the CBS limit directly applied to structural parameters, we have made use of the procedure described in ref 16 and implemented in the CFour program package.[33] More precisely, the gradient on which the geometry optimizations have been based is given by

$$\frac{\mathrm{d}E_{\mathrm{tot}}}{\mathrm{d}x} = \frac{\mathrm{d}E^{\infty}(\mathrm{HF{-}SCF})}{\mathrm{d}x} + \frac{\mathrm{d}\Delta E^{\infty}(\mathrm{CCSD(T)})}{\mathrm{d}x} \tag{6}$$

where $\mathrm{d}E^{\infty}(\mathrm{HF\text{-}SCF})/\mathrm{d}x$ and $\mathrm{d}\Delta E^{\infty}(\mathrm{CCSD(T)})/\mathrm{d}x$ are the energy gradients corresponding to the $B'' \exp(-C''n)$ extrapolation scheme for the HF-SCF energy[21] (forthcoming eq 8) and to the n^{-3} extrapolation scheme for the CCSD(T) correlation contribution[10] (forthcoming eq 7), respectively, as defined in ref 16. For the formula given above n = Q, 5, and 6 have been chosen for the HF-SCF extrapolation, and n = 5 and 6 have been used for CCSD(T). As mentioned in the Introduction, this procedure has been named as "gradient scheme".

As a sort of a numerical consistency test, for some (triatomic) molecules the near-equilibrium PES has been calculated with the above-mentioned series of correlation consistent basis sets. The range of the PES has been defined by $-0.3\ a_0 \le r - r_{\mathrm{ref}} \le +0.5\ a_0$ for bond distances and $-30° \le \theta - \theta_{\mathrm{ref}} \le +30°$ for the bond angle, where the subscript "ref" denotes the reference geometry. This has been chosen close to the corresponding CCSD(T)/cc-pV6Z optimized geometry. A total of 45−59 symmetry-unique points (the former number applies to linear cases) were computed using the MOLPRO package. To account for basis set truncation effects, at each point defining the PES an extrapolation to the CBS limit has been carried out by following a well-established approach. More precisely, the correlation contribution has been extrapolated to the complete basis limit by means of the above-mentioned n^{-3} formula:[10]

$$\Delta E^{\mathrm{corr}}(n) = \Delta E^{\mathrm{corr}}_{\infty} + A''n^{-3} \tag{7}$$

and then the Hartree−Fock complete basis limit, evaluated by the expression[20,21]

$$E^{\mathrm{SCF}}(n) = E^{\mathrm{SCF}}_{\infty} + B'' \exp(-C''n) \tag{8}$$

has been added. A polynomial function of the form

$$V(R_1,R_2,R_3) = \sum_{ijk} C_{ijk}(R_1)^i(R_2)^j(R_3)^k \tag{9}$$

has been used to accurately fit[45] the CBS energies. In eq 9 both the stretching and bending coordinates are represented by simple displacement coordinates. A full fourth-order polynomial with the symmetry allowed diagonal fifth-order terms (plus the diagonal sixth order terms only for HSC^+), which resulted in 24−41 coefficients for the CBS PES of the species considered, has been used, and the root-mean-square (rms) deviations in the fits have been found in the range 0.1−0.8 cm^{-1}. Then, the minimum of the CBS PES is the extrapolated equilibrium geometry r(CBS) as obtained by the third approach, named as "energy scheme".

Results and Discussion

The results are collected in Tables 1−4 as follows: in Table 1 are reported the results for the XSiY (X = F, Cl and Y = N, P) species, in Table 2 those for XCY (X = H, F and Y = N, P), in Table 3 those for HCS, HSC, and related cations, and in Table 4 those for most of the "standard" molecules considered in ref 16 plus a few second-row analogous systems. Values are given in Å for bond lengths and degrees for angles, and 5 decimals are used for distances and 3 for angles which means more decimals than the significative ones. This choice was made in view of the comparison of the different extrapolation procedures. Furthermore, even if beyond the scope of the present study, a comparison with the available experimental data and/

TABLE 1: Equilibrium Structure of XSiY, with X = F, Cl and Y = N, P[a]

	X−Si (Å)	Si−Y (Å)	X−Si−Y (deg)
FSiN			
MP2/6-31G*[b]	1.606	1.596	
QCISD/6-31G*[b]	1.603	1.605	147.6
CCSD(T)/cc-pVTZ[c]	1.589	1.586	
CCSD(T)/cc-pVQZ	1.58177	1.57953	
CCSD(T)/cc-pV5Z	1.57720	1.57605	
CCSD(T)/cc-pV6Z	1.57626	1.57536	
CBS: geometry scheme[d]	1.57547	1.57481	
CBS: gradient scheme[e]	1.57582	1.57485	
CBS: energy scheme[f]	1.57598	1.57487	
FSiP			
B3LYP/6-311G(2d,p)[g]	1.589	1.958	
CCSD(T)/cc-pVTZ[c]	1.590	1.977	
CCSD(T)/cc-pVQZ	1.58306	1.96803	
CCSD(T)/cc-pV5Z	1.57877	1.96327	
CCSD(T)/cc-pV6Z	1.57784	1.96224	
CBS: geometry scheme[d]	1.57716	1.96133	
CBS: gradient scheme[e]	1.57740	1.96132	
CBS: energy scheme[f]	1.57725	1.96163	
ClSiN			
MP2/6-31G*[b]	2.035	1.615	
QCISD/6-31G*[b]	2.029	1.583	
CCSD(T)/cc-pVTZ[c]	2.035	1.589	
CCSD(T)/cc-pVQZ	2.02421	1.58123	
CCSD(T)/cc-pV5Z	2.01792	1.57770	
CCSD(T)/cc-pV6Z	2.01651	1.57695	
CBS: geometry scheme[d]	2.01537	1.57632	
CBS: gradient scheme[e]	2.01540	1.57643	
CBS: energy scheme[f]	2.01565	1.57646	
ClSiP			
CCSD(T)/cc-pVTZ[c]	2.033	1.980	
CCSD(T)/cc-pVQZ	2.02271	1.96991	
CCSD(T)/cc-pV5Z	2.01691	1.96536	
CCSD(T)/cc-pV6Z	2.01551	1.96430	
CBS: geometry scheme[d]	2.01439	1.96354	
CBS: gradient scheme[e]	2.01440	1.96340	
CBS: energy scheme[f]	2.01467	1.96367	

[a] Where not explicitly reported, the ∠XSiY is 180.0 degree, i.e., the molecule is linear. [b] Reference 47. [c] Reference 48. [d] Extrapolation to CBS limit performed directly on bond distances employing eqs 1 and 2. See text. [e] Extrapolation to CBS limit performed on energy gradients employing eq 6. See text. [f] Extrapolation to CBS limit performed on energies employing eqs 7 and 8. See text. [g] Reference 53.

TABLE 2: Equilibrium Structure of XCY, with X = H, F and Y = N, P

	X−C (Å)	C−Y (Å)
HCN		
CCSD(T)/cc-pVTZ	1.06686	1.16012
CCSD(T)/cc-pVQZ	1.06686	1.15647
CCSD(T)/cc-pV5Z	1.06662	1.15567
CCSD(T)/cc-pV6Z	1.06657	1.15537
CBS: geometry scheme[a]	1.06641	1.15499
CBS: gradient scheme[b]	1.06658	1.15502
CBS: energy scheme[c]	1.06656	1.15519
Exp r_e[d]	1.06528(12)	1.15336(14)
FCN		
CCSD(T)/cc-pVTZ[e]	1.27	1.16
CCSD(T)/cc-pVQZ	1.26695	1.15951
CCSD(T)/cc-pV5Z	1.26623	1.15881
CCSD(T)/cc-pV6Z	1.26597	1.15860
CBS: geometry scheme[a]	1.26574	1.15841
CBS: gradient scheme[b]	1.26566	1.15828
CBS: energy scheme[c]	1.26576	1.15843
Exp r_e[f]	1.2641(7)	1.1568(8)
HCP		
CCSD(T)/cc-pVQZ[g]	1.07221	1.54730
CCSD(T)/cc-pV5Z[g]	1.07205	1.54446
CCSD(T)/cc-pV6Z[g]	1.07178	1.54390
CBS: geometry scheme[a,g]	1.07153	1.54357
CBS: gradient scheme[b]	1.07212	1.54334
CBS: energy scheme[c]	1.07196	1.54285
Exp r_e[h]	1.0702(10)	1.5399(2)
FCP		
CCSD(T)/cc-pVQZ[g]	1.27847	1.55178
CCSD(T)/cc-pV5Z[g]	1.27818	1.54892
CCSD(T)/cc-pV6Z[g]	1.27800	1.54824
CBS: geometry scheme[a]	1.27785	1.54761
CBS: gradient scheme[b]	1.27786	1.54774
CBS: energy scheme[c]	1.27789	1.54778
CBS+CV[g]	1.2755	1.5429
CBS+CV[i]	1.2757	1.5431
Exp r_e[i]	1.2759(4)	1.5445(2)

[a] Extrapolation to CBS limit performed directly on bond distances employing eqs 1 and 2. See text. [b] Extrapolation to CBS limit performed on energy gradients employing eq 6. See text. [c] Extrapolation to CBS limit performed on energies employing eqs 7 and 8. See text. [d] Reference 14: semiempirical equilibrium structure (from experimental ground state rotational constants and theoretical vibrational corrections). [e] Reference 49. [f] Reference 50. [g] Reference 27: “geometry scheme” used for CBS. [h] Reference 51. [i] Reference 52. CBS+CV means core valence (CV) corrections added to the CBS limit (“energy scheme”).

or previous theoretical determinations is reported in the above-mentioned tables.

The first conclusion that can be drawn is a good agreement for all the extrapolation procedures, thus providing a first validation of the “geometry scheme”. But let us go a little more into detail. First of all, we focus our attention on convergence of bond distances involving second-row atoms. From Tables 1−4, we may note that in all cases the differences are smaller than 0.0005 Å, which means within the accuracy of the level of theory considered. We note that in most cases the CBS distances derived by means of the “geometry scheme” are shorter than those obtained with the other two approaches. This seems to suggest that the extrapolation procedure directly applied to the structural parameters tends to overestimate the basis-set truncation error. Concerning bond lengths involving only first-row atoms, from Tables 2−4 it is evident that similar conclusions can be drawn. We only may note that the differences are on average smaller: this may be ascribed to the fact that the convergence is faster when only first-row elements are involved.

For bond angles, even if the data set is limited, it is apparent that the results from the different procedures well agree one with the other.

For the four open-shell species investigated we observe a good convergence as well and a good agreement of the approaches used. However, a successful comparison of CBS structures for HCS, HSC, and their cations as obtained by the “geometry” and “energy” schemes was already reported in the literature, in ref 29, but in that case a different extrapolation formula, i.e., the mixed exponential/Gaussian form by Peterson and Feller,[43,44] was employed for energies. Furthermore, for the HCCS radical and its related cation, $HCCS^+$, and anion, $HCCS^-$, a comparison between the “geometry” and “gradient” schemes were carried out in ref 32, showing a good agreement between the two approaches as well. The results mentioned for open-shell molecules do not lead to a definitive conclusion because of the limited number of cases considered, but anyway they provide an encouraging perspective for extension of extrapolation

TABLE 3: Equilibrium Structure of HCS, HSC, and Their Corresponding Cations

	H−C (Å)	C−S (Å)	∠HCS (deg)
HCS			
CCSD(T)/cc-pVQZ[a]	1.08766	1.56602	131.990
CCSD(T)/cc-pV5Z[a]	1.08723	1.56221	132.214
CCSD(T)/cc-pV6Z[a]	1.08719	1.56105	132.245
CBS: geometry scheme[a,b]	1.08715	1.55994	132.284
CBS: gradient scheme[c]	1.08754	1.56132	131.991
CBS: energy scheme[d]	1.08728	1.56027	132.096
HCS^+			
CCSD(T)/cc-pVQZ[a]	1.08220	1.48349	180.0
CCSD(T)/cc-pV5Z[a]	1.08200	1.48036	180.0
CCSD(T)/cc-pV6Z[a]	1.08200	1.47962	180.0
CBS: geometry scheme[a,b]	1.08200	1.47895	180.0
CBS: gradient scheme[c]	1.08214	1.47907	180.0
CBS: energy scheme[d]	1.08205	1.47909	180.0
	H−C (Å)	C−S (Å)	∠HCS (deg)
HSC			
CCSD(T)/cc-pVQZ[a]	1.36715	1.65171	102.886
CCSD(T)/cc-pV5Z[a]	1.36625	1.64565	103.010
CCSD(T)/cc-pV6Z[a]	1.36622	1.64416	103.039
CBS: geometry scheme[a,b]	1.36620	1.64281	103.065
CBS: gradient scheme[c]	1.36741	1.64255	103.155
CBS: energy scheme[d]	1.36660	1.64304	103.072
HSC^+			
CCSD(T)/cc-pVQZ[a]	1.39628	1.62016	74.701
CCSD(T)/cc-pV5Z[a]	1.39604	1.61602	74.320
CCSD(T)/cc-pV6Z[a]	1.39599	1.61500	74.218
CBS: geometry scheme[a,b]	1.39596	1.61411	74.121
CBS: gradient scheme[c]	1.39679	1.61418	74.127
CBS: energy scheme[d]	1.39632	1.61426	74.159

[a] Reference 29. [b] Extrapolation to CBS limit performed directly on bond distances employing eqs 1 and 2. See text. [c] Extrapolation to CBS limit performed on energy gradients employing eq 6. See text. [d] Extrapolation to CBS limit performed on energies employing eqs 7 and 8. See text.

techniques to the structures of open-shell systems with an effectiveness and reliability comparable to that well documented for closed-shell species.

A particular note is deserved for Table 5, where the results for the different functions employed in the "geometry scheme" are compared. From this table, it is evident that all extrapolation formula considered (eqs 1−5) provide reliable results as, for molecules only containing first-row elements, they agree within 0.001 Å with those obtained employing the "gradient scheme"; larger discrepancies, up to 0.003−0.004 Å, are observed when second-row atoms are involved. Analogous findings are observed for bond angles. The convergence issue is somehow expected because of the slower convergence of structural parameters involving second-row elements, but it can be overcome by using tight-d augmented basis sets,[46] which are know to speed up the convergence. Among the additional extrapolation formula considered, the mixed exponential/Gaussian function[43,44] performs better than the pure exponential function (eq 4) and the n^{-3} form of eq 5 giving discrepancies on the order of 0.0001−0.0002 Å for molecules only containing first-row elements and <0.001 Å when second-row atoms are involved. That is to say, it provides results very similar to those obtained with the "reference" approach defined by eqs 1 and 2.

As for larger molecules than those here considered, the cc-pV6Z basis may be hardly employable, we also tested the validity of the "geometry scheme" when smaller basis sets (n = T to 5) are used for extrapolating to the CBS limit. The results are collected in Table 5, and the overall conclusion is that reliable results are obtained. More precisely, for molecules containing only first-row elements, the differences on bond lengths are lower than 0.001 Å and, generally, even lower than 0.0001 Å when the mixed exponential/Gaussian function is used. In the case of species containing second-row atoms, the differences are larger, especially when the pure exponential function is employed. Of course, as discussed previously, the use of tight-d augmented basis sets is expected to reduce the discrepancies. For bond angles, the discrepancies are in general largely <0.5°. We furthermore note that the n^{-3} extrapolation formula (eq 5) applied to the case n = T and Q gives CBS distances that generally differ by less than 0.001 Å from those obtained with the "gradient scheme". This is a particularly important result for application of extrapolation procedures to large molecules.

In conclusion, a brief comment on the results obtained for the nonstandard molecules studied, i.e., those poorly investigated in the literature, is worthy of mention. The data collected in Table 1 allow us to point out how the Si−X and Si−Y bond

TABLE 4: CCSD(T) Geometrical Parameters (Bond Distances in Å, Bond Angles in deg) Compared to the Corresponding CBS Values

		CCSD(T)/			CBS		
molecule	parameter	cc-pVQZ	cc-pV5Z	cc-pV6Z	geometry scheme	gradient scheme	CCSD(T)-R12[a]
H_2O	O−H	0.95792	0.95807	0.95821	0.95839	0.95836[a]	0.95824
	∠HOH	104.118	104.374	104.425	104.484	104.478[a]	104.463
HCN	C−H	1.06686	1.06662	1.06657	1.06641	1.06658[a]	1.06656
	C−N	1.15647	1.15567	1.15537	1.15499	1.15502[a]	1.15497
HNC	N−H	0.99617	0.99626	0.99632	0.99641	0.99638[a]	0.99635
	C−N	1.17203	1.17136	1.17111	1.17082	1.17077[a]	1.17074
CO_2	C−O	1.16266	1.16211	1.16188	1.16159	1.16156[a]	1.16150
NH_3	N−H	1.01246	1.01209	1.01207	1.01210	1.01206[a]	1.01201
	∠HNH	106.183	106.514	106.585	106.631	106.641[a]	106.614
NH_2	N−H	1.02504	1.02476	1.02475	1.02476	1.02474[a]	1.02467
	∠HNH	102.721	102.951	103.009	103.071	103.060[a]	103.049
HCP	C−H	1.07221[b]	1.07206[b]	1.07178[b]	1.07153[b]	1.07212	
	C−P	1.54730[b]	1.54446[b]	1.54389[b]	1.54357[b]	1.54334	
PH_3	P−H	1.41595	1.41464	1.41452	1.41435	1.41464	
	∠HPH	93.556	93.562	93.562	93.555	93.553	
PH_2	P−H	1.41998	1.41856	1.41838	1.41825	1.41846	
	∠HPH	91.877	91.873	91.878	91.882	91.877	

[a] Reference 16. [b] Reference 27.

TABLE 5: Comparison of Different Extrapolation Formula in the Frame of the "Geometry Scheme"

		CBS/geometry scheme									
molecule	parameter	eqs 1−2/Q-5[a]	eqs 1−2/5−6	eq 3/T-5[b]	eq 3/Q-6[b]	eq 4/T-5[c]	eq 4/Q-6[c]	eq 5/T-Q[d]	eq 5/Q-5[d]	eq 5/5−6[d]	eq 6/Q-6[e]
H_2O	O−H	0.95827	0.95839	0.95817	0.95829	0.95817	0.95792	0.95767	0.95823	0.95840	0.95836[f]
	∠HOH	104.539	104.478	104.523	104.455	104.841	104.119	104.205	104.642	104.495	104.478[f]
HCN	C−H	1.06650	1.06641	1.06648	1.06653	1.06686	1.06686	1.06686	1.06637	1.06649	1.06658[f]
	C−N	1.15493	1.15499	1.15521	1.15520	1.15491	1.15647	1.15587	1.15483	1.15497	1.15502[f]
HNC	N−H	0.99632	0.99641	0.99632	0.99636	0.99627	0.99617	0.99613	0.99636	0.99641	0.99638[f]
	C−N	1.17070	1.17082	1.17099	1.17097	1.17079	1.17203	1.17146	1.17067	1.17076	1.17077[f]
CO_2	C−O	1.16159	1.16159	1.16179	1.16175	1.16167	1.16266	1.16206	1.16152	1.16157	1.16156[f]
NH_3	N−H	1.01194	1.01210	1.01188	1.01206	1.01196	1.01245	1.01218	1.01170	1.01205	1.01206[f]
	∠HNH	106.684	106.631	106.710	106.627	107.815	106.183	106.269	106.864	106.684	106.641[f]
NH_2	N−H	1.02463	1.02476	1.02460	1.02474	1.02470	1.02504	1.02473	1.02446	1.02474	1.02474[f]
	∠HNH	103.087	103.071	103.086	103.043	103.437	102.721	102.800	103.193	103.089	103.060[f]
HCP	C−H	1.07198	1.07153	1.07196	1.07162	1.07096	1.07221	1.07210	1.07189	1.07141	1.07212
	C−P	1.54292	1.54357	1.54281	1.54357	1.54036	1.54731	1.54621	1.54148	1.54312	1.54334
PH_3	P−H	1.41399	1.41435	1.41387	1.41445	1.41262	1.41595	1.41554	1.41326	1.41435	1.41464
	∠HPH	93.565	93.555	93.565	93.562	93.563	93.556	93.563	93.568	93.562	93.553
PH_2	P−H	1.41796	1.41825	1.41774	1.41827	1.41642	1.41998	1.41950	1.41708	1.41812	1.41846
	∠HPH	91.870	91.882	91.869	91.882	91.879	91.877	91.881	91.867	91.887	91.877

[a] Extrapolation to CBS limit performed directly on structural parameters employing the n^{-3} expression for correlation contributions. The values of n to which eq 1 has been applied are given. [b] Extrapolation to CBS limit performed directly on structural parameters employing the mixed exponential/Gaussian function. The values of n to which eq 3 has been applied are given. [c] Extrapolation to CBS limit performed directly on structural parameters employing the pure exponential function. The values of n to which eq 4 has been applied are given. [d] Extrapolation to CBS limit performed directly on structural parameters employing the n^{-3} expression for the whole term. The values of n to which eq 5 has been applied are given. [e] Extrapolation to CBS limit performed employing the "gradient scheme". The values of n to which eq 6 has been applied are given. [f] Reference 16.

distances vary upon Y and X substitution, respectively. We note that the Si−X (X = F, Cl) bond remains mostly unchanged (variation of about 0.001 Å) when the nitrogen atom is replaced by phosphorus; on the contrary, as clear from Table 2, the C−F and C−H distances increase by more than 0.01 and ~0.005 Å, respectively, when N is substituted by P. This different behavior can be ascribed to the increased polarization of silicon with respect to nitrogen. Similarly to Si−X, the Si−Y bond increases by less than 0.002 Å when going from X = F to X = Cl. To the best of our knowledge, there are no experimental data for the XSiY systems to compare with. From a theoretical point of view, previous investigations are limited and they were carried out at lower levels of theory. Consequently, the accuracy of the corresponding results is far from ours and a detailed comparison is not too meaningful. We only note that in the case of FSiN, the QCISD method completely fails in properly describing the molecular structure, as a bent optimized geometry was obtained.[47] Concerning XCY, experimental equilibrium structures are available in the literature[50−52] and, from the comparison of Table 2, we may note that the discrepancies observed with respect to the present CBS results are clearly due to the missing inclusion of core correlation effects. In ref 52 the near equilibrium CBS PES of FCP was derived, but as in ref 29 for HCS, HSC, and corresponding cations, the mixed exponential/Gaussian function[43,44] was employed in energy extrapolation. Furthermore, a systematic basis-set investigation on XBS and XCP, with X = H, F, Cl, was previously carried out, and we refer interested readers to ref 27 for all details.

Concluding Remarks

The present study reports the first systematic validation of the extrapolation to the CBS limit directly applied to structural parameters by means of a well-tested and theoretically justified scheme. The main conclusion that can be drawn is that the "geometry scheme", even if empirically based, provides reliable results and is therefore the more costly effective approach for obtaining CBS equilibrium geometries. Different extrapolation functions have been compared in the frame of the "geometry scheme", leading at the conclusion that the n^{-3} and mixed exponential/Gaussian procedures, expressed by eqs 1 and 2 and eq 3, respectively, provide the best results in very good agreement with the "gradient scheme". Furthermore, we may point out that good results are obtained even when the "geometry scheme" is applied to smaller basis sets.

The present work should be considered as the first step of a wider project. Further investigations, involving a larger set of molecules, also including a significative number of radical species and ionic systems, as well as larger molecules than triatomics and tetratomics are required to widen the data set with the aim of providing a significative statistical analysis.

Finally, as is clear from refs 48 and 54, for the XSiY species the investigation of the XSiY−XYSi isomerization is of great interest because these systems are isovalent to the well-studied HCN−HNC system and, on the other hand, for them it is not so clear which isomer is the most stable. This information would also be useful in view of improving the knowledge on silicon-containing species. Work is in progress in such a direction.

Acknowledgment. This work has been supported by University of Bologna (RFO funds). The author thanks the CINECA supercomputing center for a grant of computer time on the IBM SP5 machine. The author gratefully thanks Profs. J. Gauss and J. F. Stanton for fruitful discussions, as well as the reviewers for enlightening remarks.

References and Notes

(1) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479–483.

(2) Helgaker, T.; Gauss, J.; Jørgensen, P.; Olsen, J. *J. Chem. Phys.* **1997**, *106*, 6430–6440.

(3) Bak, K. L.; Gauss, J.; Jørgensen, P.; Olsen, J.; Helgaker, T.; Stanton, J. F. *J. Chem. Phys.* **2001**, *114*, 6548–6556.

(4) Coriani, S.; Marchesan, D.; Gauss, J.; Hätting, C.; Helgaker, T.; Jørgensen, P. *J. Chem. Phys.* **2001**, *123*, 184107/1−12.

(5) Halkier, A.; Helgaker, T.; Jørgensen, P.; Klopper, W.; Koch, H.; Olsen, J.; Wilson, A. K. *Chem. Phys. Lett.* **1998**, *286*, 243–252.

(6) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007–1023.

(7) Wilson, A. K.; van Mourik, T.; Dunning, T. H., Jr. *J. Mol. Struct. (THEOCHEM)* **1996**, *388*, 339–349.

(8) Martin, J. M. L. *Chem. Phys. Lett.* **1996**, *259*, 669–678.

(9) Wilson, A. K.; Dunning, T. H., Jr. *J. Chem. Phys.* **1997**, *106*, 8718–8726.

(10) Helgaker, T.; Klopper, W.; Koch, H.; Noga, J. *J. Chem. Phys.* **1997**, *106*, 9639–9646.

(11) Halkier, A.; Helgaker, T.; Jørgensen, P.; Klopper, W.; Olsen, J. *Chem. Phys. Lett.* **1999**, *302*, 437–446.

(12) Feller, D. J.; Sordo, J. A. *J. Chem. Phys.* **2000**, *113*, 485–493.

(13) Bak, K. L.; Jørgensen, P.; Olsen, J.; Helgaker, T.; Koppler, W. *J. Chem. Phys.* **2000**, *112*, 9229–9242.

(14) Pawłowski, F.; Jørgensen, P.; Olsen, J.; Hegelund, F.; Helgaker, T.; Gauss, J.; Bak, K. L.; Stanton, J. F. *J. Chem. Phys.* **2002**, *116*, 6482–6496.

(15) Pawłowski, F.; Halkier, A.; Jørgensen, P.; Bak, K. L.; Helgaker, T.; Koppler, W. *J. Chem. Phys.* **2002**, *118*, 2539–2549.

(16) Heckert, M.; Kállay, M.; Tew, D. P.; Klopper, W.; Gauss, J. *J. Chem. Phys.* **2006**, *125*, 044108/1−10.

(17) Heckert, M.; Kállay, M.; Gauss, J. *Mol. Phys.* **2005**, *103*, 2109–2115.

(18) Noga, J.; Kutzelnigg, W. *J. Chem. Phys.* **1994**, *101*, 7738–7762.

(19) Klopper, W. In *Encyclopedia of Computational Chemistry*; Schleyer, P. v. R., Allinger, N. L., Clark, T., Gasteiger, J., Kollmann, P. A., Schaefer, H. F., III, Schreiner, P. R., Eds.; Wiley: New York, 1998; pp 2351ff.

(20) Feller, D. *J. Chem. Phys.* **1992**, *96*, 6104–6114.

(21) Feller, D. *J. Chem. Phys.* **1993**, *98*, 7059–7071.

(22) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *99*, 1914–1929.

(23) Peterson, K. A.; Dunning, T. H., Jr. *J. Mol. Struct. (THEOCHEM)* **1997**, *400*, 93–117.

(24) Martin, J. M. L.; Taylor, P. R. *Chem. Phys. Lett.* **1996**, *248*, 336–344.

(25) Persson, B. J.; Taylor, P. R.; Martin, J. M. L. *J. Phys. Chem. A* **1998**, *102*, 2483–2492.

(26) Puzzarini, C. *Phys. Chem. Chem. Phys.* **2003**, *5*, 26–30.

(27) Puzzarini, C. *Phys. Chem. Chem. Phys.* **2004**, *6*, 344–351.

(28) Puzzarini, C.; Gambi, A. *J. Chem. Phys.* **2005**, *122*, 064316/1−10.

(29) Puzzarini, C. *J. Chem. Phys.* **2005**, *123*, 024313/1−14.

(30) Puzzarini, C.; Peterson, K. A. *Chem. Phys.* **2005**, *311*, 177–186.

(31) Puzzarini, C.; Cazzoli, G.; Gambi, A.; Gauss, J. *J. Chem. Phys.* **2006**, *125*, 054313/1−8.

(32) Puzzarini, C. *Chem. Phys.* **2008**, *346*, 45–52.

(33) Stanton, J. F.; Gauss, J.; Harding, M. E.; Szalay, P. G. *CFOUR A quantum chemical program package*; Auer, A. A., Bartlett, R. J., Benedikt, U., Berger, C., Bernholdt, D. E., Christiansen, O., Heckert, M., Heun, O., Huber, C., Jonsson, D., Jusélius, J., Klein, K., Lauderdale, W. J., Matthews, D., Metzroth, T., O'Neill, D. P., Price, D. R., Prochnow, E., Ruud, K., Schiffmann, F., Stopkowicz, S., Tajti, A., Varner, M. E., Vázquez, J., Wang, F., Watts, J. D., contributors; and the integral packages MOLECULE (Almlöf, J.; Taylor, P. R.), PROPS (Taylor, P. R.), ABACUS (Helgaker, T.; Jensen, H. J. Aa.; Jørgensen, P.; Olsen, J.), and ECP routines by A. V. Mitin and C. van Wüllen. For the current version, see http://www.cfour.de.

(34) Werner, H.-J.; Knowles, P. J. *MOLPRO, a package of ab initio programs*; Almlöf, J., Amos, R. D., Berning, A., Deegan, M. J. O., Eckert, F., Elbert, S. T., Hampel, C., Lindh, R., Meyer, W., Nicklass, A., Peterson, K., Pitzer, R., Stone, A. J., Taylor, P. R., Mura, M. E., Pulay, P., Schütz, M., Stoll, H., Thorsteinsson, T., Cooper, D. L., contributors.

(35) Werner, H.-J.; Knowles, P. J. *J. Chem. Phys.* **1985**, *82*, 5053–5063.

(36) Knowles, P. J.; Werner, H.-J. *Chem. Phys. Lett.* **1985**, *115*, 259–267.

(37) Lee, T. J.; Taylor, P. R. *Int. J. Quantum Chem. Symp.* **1989**, *23*, 199–207.

(38) Lee, T. J.; Scuseria, G. E. In *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy*, Langhoff, S. R., Ed.; Kluwer: Dordrecht, The Netherlands, 1995, pp 47ff.

(39) Leininger, M. L.; Nielsen, I. M. B.; Crawford, T. D.; Janssen, C. L. *Chem. Phys. Lett.* **2000**, *328*, 431–436.

(40) Eckert, F.; Pulay, P.; Werner, H.-J. *J. Comput. Chem.* **1997**, *18*, 1473–1483.

(41) El Azhary, A.; Rauhut, G.; Pulay, P.; Werner, H.-J. *J. Chem. Phys.* **1998**, *108*, 5185–5193.

(42) The use of the MOLPRO code for this part of the work was only dictated by the availability of a computer-time grant at CINECA, supercomputing center. Therefore, there is no implication that the employment of numerical gradients is the most efficient choice for geometry optimizations.

(43) Peterson, K. A.; Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1994**, *100*, 7410–7415.

(44) Feller, D.; Peterson, K. A. *J. Chem. Phys.* **1999**, *110*, 8384–8396.

(45) Senekowitsch, J. Ph. D. thesis. Universität Frankfurt, Frankfurt, Germany, 1988.

(46) Dunning, T. H., Jr.; Peterson, K. A.; Wilson, A. K. *J. Chem. Phys.* **2001**, *114*, 9244–9253.

(47) Apeloig, Y.; Albrecht, K. *J. Am. Chem. Soc.* **1995**, *117*, 7263–7264.

(48) Bhattacharyya, I.; Bera, N. C.; Das, A. K. *Int. J. Quantum Chem.* **2008**, *108*, 447–455.

(49) Bhattacharyya, I.; Bera, N. C.; Das, A. K. *Eur. Phys. J. D* **2007**, *42*, 221–227.

(50) Degli Esposti, C.; Favero, P. G.; Serenellini, S.; Cazzoli, G. *J. Mol. Struct.* **1982**, *82*, 221–236.

(51) Puzzarini, C.; Tarroni, R.; Palmieri, P.; Demaison, J.; Senent, M. L. *J. Chem. Phys.* **1996**, *105*, 3132–3141.

(52) Bizzocchi, L.; Degli Esposti, C.; Puzzarini, C. *Mol. Phys.* **2006**, *104*, 2627–2640.

(53) Driess, M.; Monsé, C.; Bläser, D.; Boese, R.; Bornemann, H.; Kuhn, A.; Sander, W. *J. Organomet. Chem.* **2003**, *686*, 294–305.

(54) Lind, M. C.; Pickard, F. C.; Ingles, J. B.; Paul, A.; Yamaguchi, Y.; Schaefer, H. F., III, *J. Chem. Phys.* **2009**, *130*, 104301/1–13.

JP9040327