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Polarization-Consistent versus Correlation-Consistent Basis Sets in Predicting Molecular and Spectroscopic Properties

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Compared to the correlation-consistent basis sets, it is not known if polarization-consistent pc-*n* basis sets, which were initially developed for HF and DFT calculations, can provide a monotonic and faster convergence toward the basis-set limit for results at *correlated* levels as well as better accuracy for a similar number of basis functions. It is also not known whether the pc-*n* basis sets can compute second derivatives of energy, such as nuclear magnetic shielding tensors, efficiently. To address these questions, the pc-*n* ($n = 1-4$), cc-pV*x*Z, and/or aug-cc-pV*x*Z (x = D, T, Q, 5, and 6) basis sets were used to compute the molecular and/or spectroscopic parameters of H_2, H_2O, and NH_3 at the RHF, B3-LYP, MP2, and/or CCSD(T) levels of theory. The results show that compared to the cc-pV*x*Z and/or aug-cc-pV*x*Z basis sets the pc-*n* basis sets yield faster convergence toward the basis-set limit but equivalent molecular and/or spectroscopic parameters in the basis-set limit at the RHF, DFT, MP2, and CCSD(T) levels. Because the pc-*n* basis sets show faster convergence, fewer basis-set functions are needed to reach the accuracy obtained with the aug-cc-pV*x*Z basis sets, enabling faster calculations and less computer storage space. The results also show that the pc-*n* basis sets, in conjunction with the "locally dense" basis-set approach, could be applied to predict accurate parameters; thus, they could be used to estimate accurate molecular or spectroscopic properties (e.g., NMR parameters) for larger systems such as the active site of enzymes.

Introduction

Ab initio calculations often support a deeper understanding of experimental data; for example, ab initio calculated NMR parameters have been used routinely to support analysis of experimental spectra.[1−3] The reliability of ab initio calculations depends partly on the complexity of the system studied. For fairly small molecular systems, ab initio thermochemical results with chemical accuracy (1−2 kcal/mol) are currently feasible. Notably, the coupled-cluster method CCSD(T), with single and double excitations augmented by a perturbative correction for triple excitations, has reached an accuracy close to full configuration interaction for a given basis set.[4,5] For larger molecules, trends or changes in the ab initio parameters are often helpful, and approximations are usually made to gain valuable insight. Such approximations often rely on accidental error cancellations and could give fairly accurate results. For example, predicted chemical shifts are obtained by subtracting the corresponding parameters calculated for a small reference molecule at the same level of theory, in analogy to the routine use of tetramethylsilane (TMS) in experimental proton and carbon NMR spectroscopy.[3,6−9] Thus, the accuracy of the absolute ab initio parameters could be critical because they could change the predicted relative trends.

The accuracy of absolute ab initio parameters obviously depends on the method employed.[4,5,10−13] Currently, it is not the wave function (i.e., theory level) but the basis set that limits the accuracy of the ab initio parameters.[14,15] Although the complete basis set (CBS) limit approach with Dunning's correlation-consistent (cc-pV*x*Z/aug-cc-pV*x*Z) basis sets[16−21] yields accurate molecular energetic and spectroscopic parameters, its practical use is currently limited to fairly small molecular systems.[22] Thus, its use to study energetics of biomolecules is presently impractical because the CPU time of restricted Hartree−Fock (RHF), Möller−Plesset perturbation to second order (MP2), and CCSD(T) calculations scales roughly as N^4, N^5, and N^7, respectively,[10,23,24] where N is the number of basis functions. Compared to the correlation-consistent basis sets, Jensen's polarization-consistent pc-*n* basis sets provide not only a monotonic but also a faster convergence toward the CBS limit for density functional theory (DFT) and/or RHF energies, dipole moments, polarizabilities, geometries, and harmonic frequencies of small molecules such as H_2, N_2, CO, O_2, HF, and HCl; they also provide better accuracy for a similar number of basis functions.[25−31] However, it is not known whether the pc-*n* basis sets, which were designed for HF and DFT calculations, could (i) yield results at *correlated* levels that smoothly converge faster to the CBS limit than the aug-cc-pV*x*Z basis sets, and are as accurate, and (ii) efficiently yield second derivatives of energy such as nuclear magnetic shielding tensors.

Herein, both the pc-*n* and aug-cc-pV*x*Z basis sets are used to compute selected molecular properties including geometries, harmonic frequencies, dipole moments, energies, and/or NMR parameters of hydrogen, water, and ammonia at the RHF, MP2, B3-LYP, and/or CCSD(T) levels of theory. The CBS convergence patterns and values in the CBS limit obtained with both basis-set families are compared. Hydrogen, water, and ammonia have been chosen for study because accurate experimental data[32,33] and/or benchmark theoretical studies[33−36] are available for comparison with the results herein. Furthermore, H_2 was

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selected because of the difficulties in regularly converging and accurately predicting its NMR parameters,[37,38] while water was chosen because of its importance in biological systems. Ammonia was selected because it serves as a reference for predicted NMR chemical shifts, and its nitrogen isotropic shielding could be used as a reference for chemical shift calculations involving imidazole, which model the histidine side chain. Its ^{15}N NMR parameters were computed using the "locally dense" approach,[9,39,40] where large basis sets such as pc-*n* and aug-cc-pV*x*Z are applied to individual atoms of interest in a big molecule (e.g., N), while a much smaller basis set is applied to the remaining atoms.

Methodology. All calculations were performed using the Gaussian03 program,[41] except the CCSD(T) NMR parameters, which were obtained using the ACESII Mainz-Austin-Budapest program (http://www.aces2.de).[42] The calculations employed the cc-pV*x*Z and/or aug-cc-pV*x*Z (x = D, T, Q, 5, and, in some cases, 6) and pc-*n* (n = 1, 2, 3, and 4) basis sets, where *n* indicates the polarization level beyond the isolated atom.

Geometry Optimization. Using the cc-pV*x*Z and/or aug-cc-pV*x*Z and pc-*n* basis-set families, fully optimized geometries and frequencies of H_2 were computed using MP2 and CCSD(T), while those of H_2O were computed using RHF,[43] B3-LYP,[44,45] MP2,[46] and CCSD(T).[47] Because of computer memory limitations, the MP2 and CCSD(T) harmonic frequencies of water could not be obtained with the largest aug-cc-pV6Z and pc-4 basis sets. Ammonia was fully optimized at the B3-PW91/6-311++G** level.[48,49]

GIAO-NMR Calculations. For each H_2 or H_2O geometry fully optimized at a given level of theory and basis set, say MP2/cc-pVDZ, single-point gauge-including atomic orbital (GIAO) calculations[7,8,50] were carried out at the same level. GIAO-CCSD(T) calculations were performed using only the cc-pV*x*Z and/or aug-cc-pV*x*Z basis sets because the pc-*n* basis sets have not been implemented in the AcesII program. Because of memory limitations, only RHF and B3-LYP NMR parameters were obtained with the largest aug-cc-pV6Z and pc-4 basis sets. On the basis of the B3−PW91/6-311++G** NH_3 geometry, single-point GIAO-NMR calculations were carried out using RHF and B3-PW91 with both unified basis sets on N and H atoms as well as the locally dense aug-cc-pV*x*Z or pc-*n* basis sets on N but a smaller 6-31G* basis set on H.

CBS Calculations. The molecular property, $Y(x)$, was extrapolated to the CBS limit, $Y(\infty)$, by fitting the results to three-parameter[34,35] and two-parameter functions:[36,51]

$$Y(x) = Y(\infty) + A \exp(-x/B) \qquad (1)$$

$$Y(x) = Y(\infty) + A/x^3 \qquad (2)$$

The extrapolated value $Y(\infty)$ corresponds to the best estimate of the predicted property for infinite zeta (or cardinal number "x"), and A and B are fitted parameters. All results herein are derived from eq 1, except for some of the fits with a smaller number of points in the Supporting Information, which employ eq 2.

For molecular properties such as energy that display a smooth systematic convergence with increasing x, data for all x were fitted to obtain the CBS limit, $Y(\infty)$;[35,37,38] in such cases, using all x data points also allows better graphical illustration of the systematic convergence of the molecular property (see Figures 1 and 2). Note that for plotting and fitting purposes, we have redefined pc-*n* (n = 1, 2, 3, and 4) to be equivalent to pc-*x* (x = 2, 3, 4, 5), respectively; for example, pc-1 is equivalent to pc-2 and pc-4 to pc-5. For molecular properties such as second derivatives of energy that sometimes display an irregular convergence with increasing x, especially for less-accurate and less-flexible basis sets ($x = 2$ and/or 3), only data corresponding to higher x values were fitted to obtain the CBS limit.[37,38] Because we are interested in comparing molecular properties obtained with selected wave functions and at different optimized geometries, we fitted the total values instead of separating them into the SCF and correlation components, which is often used when studying SCF and correlated energy convergence at the experimental geometry[36,52] or at a selected optimized geometry.

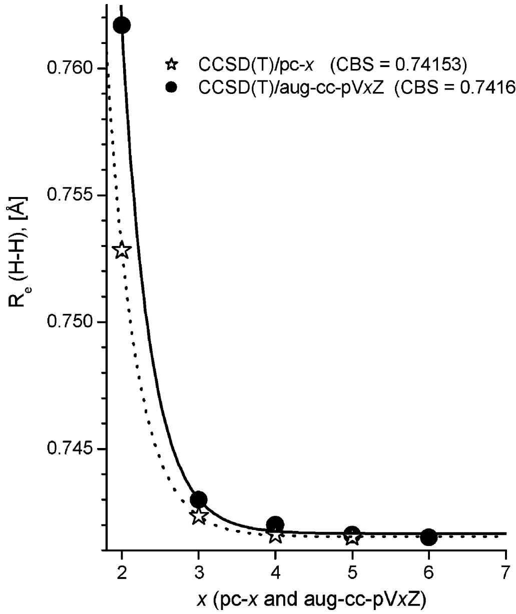

Figure 1. Convergence of the equilibrium hydrogen distance (R_e) calculated using the CCSD(T) method with pc-*n* (Π) and aug-cc-pV*x*Z (●) basis sets. The curves are obtained by fitting the computed values to eq 1, and the CBS values are reported in Table 1. Note that pc-*x* (x = 2, 3, 4, 5) is equivalent to pc-*n* (n = 1, 2, 3, and 4), respectively.

Results and Discussion

H_2. To assess which basis-set family yields a faster convergence of a given molecular property, the convergence patterns of CCSD(T)-calculated H_2 equilibrium bond distances, R_e, obtained with both pc-*n* and aug-cc-pV*x*Z basis sets are compared in Figure 1. As the CBS limit is approached (increasing x in Figure 1), the molecular properties computed with the pc-*n* basis sets generally converge slightly faster than those computed using the aug-cc-pV*x*Z basis sets (see also Supporting Information Figure 1). In other words, for a given x, the property calculated with the pc-*n* basis set is closer to the CBS limit than that computed with the cc-pV*x*Z or aug-cc-pV*x*Z basis set. Additionally, much less computer time and memory are needed for the H_2 calculations using the pc-*n* basis sets, as compared to the cc-pV*x*Z or aug-cc-pV*x*Z basis sets. For example, the H−H bond length predicted with pc-4 (176 basis functions) is similar to that obtained with aug-cc-pV6Z (254 basis functions).

To evaluate if a given molecular property computed using the pc-*n* basis sets not only converges faster but is also as accurate as that calculated with the cc-pV*x*Z or aug-cc-pV*x*Z basis sets, the errors in the H−H interatomic distance, harmonic vibration frequency, energy, and rovibrationally corrected isotropic shielding computed at correlated levels using the three basis-set families in the CBS limit are listed in Table 1. At a given correlated level (CCSD(T) or MP2), all three basis-set

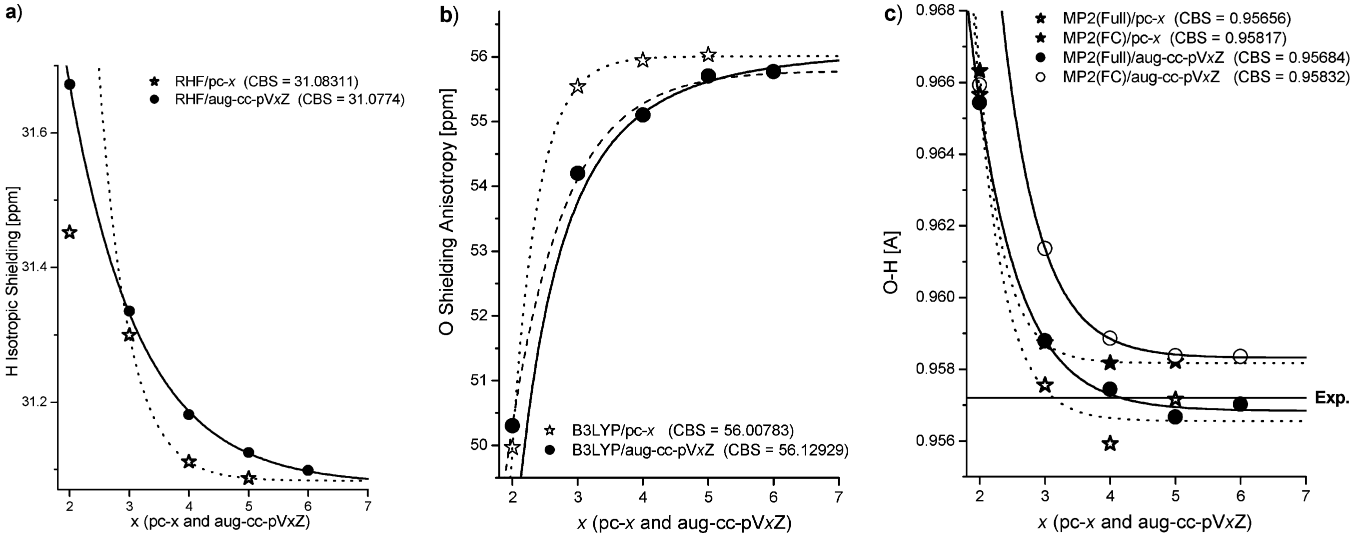

Figure 2. Convergence of selected water molecular properties calculated using pc-*n* (Π) and aug-cc-pV*x*Z (●) basis sets: (a) GIAO-RHF hydrogen isotropic shielding (σ_H, ppm), (b) GIAO-B3-LYP oxygen shielding anisotropy ($\Delta\sigma_O$, ppm), and (c) MP2 O−H bond length (Å) with frozen core (FC) and all core electrons correlated (Full). Note that pc-*x* (*x* = 2, 3, 4, 5) is equivalent to pc-*n* (*n* = 1, 2, 3, and 4), respectively. The curves were obtained by fitting the computed values to eq 1, and the CBS values are reported in Tables 2 and 3. In Figure 2b, the dashed curves were obtained by fitting five aug-cc-pV*x*Z (*x* = 2−6) points, and the solid curves were obtained by fitting the last three points (*x* = 4−6).

TABLE 1: MP2 and CCSD(T) Molecular and Spectroscopic Parameters of H_2 Calculated Using Correlation/Polarization-Consistent Basis Sets in the CBS Limit and Their Deviations from Experiment

method	MP2			CCSD(T)			experiment
basis set	cc-pV*x*Z	aug-cc-pV*x*Z	pc-*n*	cc-pV*x*Z	aug-cc-pV*x*Z	pc-*n*	(expt)
R_e(H−H) (Å)	0.73582	0.73596	0.73570	0.74160	0.74166	0.74153	0.74144[a]
$R_e - R_e^{expt}$	−0.00562	−0.00548	−0.00574	0.00016	0.00022	0.00009	0
ω_o (cm^{-1})	4520.33	4517.08	4517.88	4405.01	4405.29	4405.11	4401.21[a]
$\omega_o - \omega_o^{expt}$	119.12	115.87	116.67	3.80	4.08	3.90	0
E (hartree)	−1.16746	−1.16751	−1.16739	−1.17429	−1.17430	−1.17426	−1.17448[b]
$E - E^{expt}$	7.02×10^{-3}	6.97×10^{-3}	7.09×10^{-3}	0.19×10^{-3}	0.18×10^{-3}	0.22×10^{-3}	0
σ (ppm)[c]	26.3691	26.3708	26.3538	26.2893	26.2900	26.2535[d]	26.2886[e]
$\sigma - \sigma^{expt}$	0.0805	0.0822	0.0652	0.0007	0.0014	−0.0351[d]	0

[a] From Huber and Herzberg, 1979.[32] [b] From Sims and Hagstrom, 2006.[53] [c] Using a rovibrational and thermal correction of −0.3686 ppm for 296 K from Sundholm and Gauss, 1997.[54] [d] GIAO-MP2 at CCSD(T) geometry (see the methods section). [e] From Sundholm and Gauss, 1997.[54]

families in the CBS limit yield results converging to essentially the same value and predict accurate H_2 parameters. For example, the cc-pV*x*Z, aug-cc-pV*x*Z, and pc-*n* basis sets in the CBS limit predict nearly identical CCSD(T) H−H bond distances of 0.74160, 0.74166, and 0.74153 Å, respectively, which reproduce the experimental value[32] (0.74144 Å) to within 0.00022 Å. They also predict nearly identical CCSD(T) harmonic vibrational frequencies ($\omega_o = 4405$ cm^{-1}) in the CBS limit that are within ~4 cm^{-1} of the experimental frequency[32] ($\omega_o^{expt} = 4401$ cm^{-1}). Because the experimental H_2 energy is not available, the current best calculation of the Born−Oppenheimer energy (−1.174 475 931 399 hartree)[53] using Kolos−Wolniewicz (also known as Hylleraas) wave function at the experimental H−H distance of 0.74144 Å was used as a reference. All three basis-set families in the CBS limit yield CCSD(T) energies that deviate from this reference by at most 0.22 millihartree. In the CBS limit, the cc-pV*x*Z and aug-cc-pV*x*Z basis sets yield CCSD(T) isotropic shieldings including rovibrational and thermal corrections ($\sigma \sim 26.29$ ppm) that are within 0.0014 ppm of the experimental value[54] ($\sigma^{expt} = 26.2886$ ppm). Although the corresponding CCSD(T) σ value derived from the pc-*n* basis sets could not be obtained (see the methods section), the corresponding MP2 value ($\sigma = 26.25$ ppm) computed using the CCSD(T) H_2 geometry is still close to the measured number (within 0.04 ppm).

The absolute accuracy of a given molecular property, as measured by the deviation from the experimental value, depends on the theory level rather than the basis-set family in the CBS limit. For all of the properties listed in Table 1, the CCSD(T) CBS estimates are closer to the respective experimental values than the corresponding MP2 numbers. In the CBS limit of the cc-pV*x*Z, aug-cc-pV*x*Z, and pc-*n* basis sets, MP2 underestimates the H−H bond length by ~0.006 Å, whereas CCSD(T) overestimates the bond length only slightly (by 0.0001−0.0002 Å). Furthermore, MP2 overestimates the harmonic vibrational frequency, energy, and isotropic shielding by about 116−119 cm^{-1}, ~7 millihartree, and 0.07−0.08 ppm, respectively, whereas CCSD(T) decreases the corresponding errors significantly to only ~4 cm^{-1}, ~0.2 millihartree, and <0.002 ppm. Because the CCSD(T) structure is more accurate than the MP2 structure (see above), the GIAO-MP2/pc-*n* hydrogen isotropic shielding evaluated at the CCSD(T) geometry (26.25 ppm) is closer to the experimental value (26.29 ppm) than that evaluated at the MP2 geometry (26.35 ppm), underscoring the impact of accurate geometry on the isotropic shielding.

The usefulness of the CBS approach in obtaining accurate absolute values is apparent from comparing the results herein with the most recent “benchmarks” in previous works. At the CCSD(T) level, the errors in the CBS predicted H−H bond lengths ($0.9-2.2 \times 10^{-4}$ Å, Table 1) are less than the error in the cc-pCVQZ predicted value (4.6×10^{-4} Å).[33] Likewise, at the CCSD(T) level, the CBS rovibrationally corrected isotropic shielding value computed with the cc-pV*x*Z basis sets deviate

TABLE 2: Deviations of aug-cc-PV*x*Z or pc-*n* CBS Water Ground-State Geometry, Dipole Moment, Energy, and Harmonic Frequencies Calculated Using Various Methods from Experiment

CBS basis	RHF	B3-LYP	MP2-FC[a]	MP2	CCSD(T)-FC[a]	CCSD(T)
			O−H[b] (Å)			
aug-cc-pV*x*Z	−0.0176	0.0032	0.0011	−0.0004	0.0003	−0.0005
pc-*n*	−0.0155	0.0032	0.0009	−0.0007	0.0011	−0.0016
			H$\hat{\mathrm{O}}$H[b] (deg)			
aug-cc-pV*x*Z	1.82	0.61	−0.09	0.08	0.05	0.08
pc-*n*	1.81	0.61	−0.23	−0.07	−0.15	0.02
			μ[c] (D)			
aug-cc-pV*x*Z	0.0811	−0.0086	0.1289	0.1244	0.1279	0.1252
pc-*n*	0.0812	−0.0083	0.1297	0.1236	0.1267	0.1202
			energy[d] (mH)			
aug-cc-pV*x*Z	371.55	−34.50	75.35	27.48	66.72	18.38
pc-*n*	371.83	−34.37	75.56	1.50	63.67	−21.53
			$\omega_1(\delta_{\mathrm{HOH}})$[e] (cm^{-1})			
aug-cc-pV*x*Z	99.62	−18.96	−15.07	−11.68	5.76	13.59
pc-*n*	99.78	−19.30	[f]	[f]	[f]	[f]
			$\omega_2(\nu_{\mathrm{OHsym}})$[e] (cm^{-1})			
aug-cc-pV*x*Z	298.02	−25.10	22.56	17.43	13.68	9.07
pc-*n*	297.78	−25.53	[f]	[f]	[f]	[f]
			$\omega_3(\nu_{\mathrm{OHasym}})$[e] (cm^{-1})			
aug-cc-pV*x*Z	288.45	−33.50	27.68	35.61	13.23	9.95
pc-*n*	288.20	−34.00	[f]	[f]	[f]	[f]

[a] FC denotes calculations with a frozen core. [b] Experimental O−H = 0.9572(3) Å and H$\hat{\mathrm{O}}$H = 104.52(5)°.[58,59] [c] Experimental dipole moment μ = 1.8546(6) D.[60,61] [d] "Experimental" nonrelativistic energy $E = -76.440$ hartree.[36,52] [e] Experimental harmonic frequencies: $\omega_1 = 1648.47$ cm^{-1}, $\omega_2 = 3832.17$ cm^{-1}, and $\omega_3 = 3942.53$ cm^{-1}.[32,58] [f] CBS value could not be obtained because the data for the larger pc-3 and/or pc-4 basis sets could not be obtained (see Supporting Information Figures S4 and S5).

TABLE 3: Deviations of aug-cc-pV*x*Z or pc-*n* CBS Water NMR Parameters (ppm) Calculated Using Various Methods from Experiment

CBS basis	RHF	B3-LYP	MP2(FC)	MP2
		σ_O[a]		
aug-cc-pV*x*Z	2.08	−9.66	10.47	11.26
pc-*n*	2.35	−9.15	9.55	10.53
		$\Delta\sigma_O$[b]		
aug-cc-pV*x*Z	7.62	7.23	−3.19	−3.17
pc-*n*	7.90	7.11	−2.67	−2.60
		σ_H[c]		
aug-cc-pV*x*Z	0.54	0.30	−0.35	−0.21
pc-*n*	0.54	0.31	−0.32	−0.29
		$\Delta\sigma_H$[d]		
aug-cc-pV*x*Z	1.84	−0.48	1.03	1.07
pc-*n*	1.87	−0.43	1.05	1.23

[a] Experimental rovibrationally and temperature-corrected oxygen isotropic shielding σ_O = 323.6 ppm;[62] MCSCF calculated rovibration and temperature corrections for oxygen isotropic shielding = −10.93 ppm.[63] [b] MCSCF calculated oxygen shielding anisotropy $\Delta\sigma_O$ = 46.94 ppm;[64] MCSCF calculated rovibration and temperature corrections for oxygen shielding anisotropy = −1.96 ppm.[63] [c] Experimental rovibrationally and temperature-corrected hydrogen isotropic shielding σ_H = 30.052(15);[65] MCSCF calculated rovibration and temperature corrections for hydrogen isotropic shielding = −0.49 ppm.[63] [d] Experimental hydrogen shielding anisotropy $\Delta\sigma_H$ = 19.078 ppm.[64] MCSCF calculated rovibration and temperature corrections for hydrogen shielding anisotropy = −0.99 ppm.[63]

from the experimental number by 0.0007 ppm (Table 1), whereas the corresponding value computed with the 8s4p3d2f basis (26.2983 ppm)[54] deviates by an order of magnitude more (0.01 ppm). At the MP2 level, the CBS energy (−1.1675 hartree) obtained by fitting all five aug-cc-pV*x*Z (x = 2, 3, 4, 5, and 6) energies is closer to the best energy estimate (−1.1745 hartree) than that (−1.1672 hartree) obtained by a less-complete fit of the aug-cc-pV*x*Z (x = 2, 3, 4) energies.[55]

H_2O. Because RHF, B3-LYP, MP2, and CCSD(T) convergence patterns of water properties (geometry, harmonic frequencies, and NMR parameters) using *both* pc-*n* and aug-cc-pV*x*Z basis sets have not been compared in the literature, we have evaluated their convergence patterns (see Figure 2 and Supporting Information Figures 2−5). As observed for H_2, the pc-*n* basis sets generally yield faster convergence of the water properties than the aug-cc-pV*x*Z basis sets. For example, the pc-*n* basis sets exhibit faster convergence than the aug-cc-pV*x*Z basis sets for the RHF hydrogen isotropic shielding (Figure 2a), B3-LYP oxygen shielding anisotropy (Figure 2b), and MP2 water O−H bond length (Figure 2c). The convergence rate is practically determined by the maximum number of the aug-cc-pV*x*Z and pc-*n* basis functions, which is 443 for the aug-cc-pV*6*Z basis set and 321 for the pc-4 basis set. However, both basis-set families yield similar results in the CBS limit (see below); hence, water properties computed with the pc-*n* basis sets generally converge faster than those computed with the aug-cc-pV*x*Z basis sets.

To evaluate if in the CBS limit the pc-*n* derived results are as accurate as the aug-cc-pV*x*Z derived ones, the errors in the water O−H bond length, H$\hat{\mathrm{O}}$H bond angle, dipole moment, energy, harmonic frequencies, and O/H rovibrationally corrected isotropic shieldings and shielding anisotropies were computed with both basis-set families in the CBS limit at various theory levels (see Tables 2 and 3). For a given theory level, both aug-cc-pV*x*Z and pc-*n* basis sets in the CBS limit yield equivalent geometries, dipole moments, energies, and spectroscopic parameters for water, as evidenced by the similar errors. For example, both aug-cc-pV*x*Z and cc-pV*x*Z basis sets in the CBS limit yield nearly identical errors in the B3-LYP O−H bond length (0.0032 Å), H$\hat{\mathrm{O}}$H bond angle (0.61°), dipole moment (−0.008 D), energy (−0.034 hartree), H$\hat{\mathrm{O}}$H bending frequency (−19 cm^{-1}), O−H symmetric stretching frequency (−25 cm^{-1}), and O−H asymmetric stretching frequency (−34 cm^{-1}) (see Table 2). The aug-cc-pV*x*Z and pc-*n* basis sets in the CBS limit also yield similar errors in the B3-LYP oxygen (∼ −9 ppm) or hydrogen (0.3 ppm) isotropic shieldings and oxygen (7 ppm) or hydrogen (∼ −0.4 ppm) shielding anisotropies (see Table 3).

As for hydrogen, the absolute accuracy of a given water property, as measured by the deviation from the respective experimental value, depends on the theory level rather than the basis-set family in the CBS limit. Except for the water dipole moment, oxygen isotropic shielding and hydrogen shielding anisotropy, whose values could not be obtained with the largest cc-pV6Z and/or pc-4 basis set, CCSD(T) and MP2 yield CBS estimates using the cc-pV*x*Z basis set that are closer to the experimental value than the RHF and/or B3-LYP methods. MP2 yields a more accurate oxygen shielding anisotropy than B3-LYP (Table 3) because DFT overestimates the paramagnetic component of heavy nuclei shieldings.[37,38,56,57] Incorporating electron correlation effects significantly improves the water energy and harmonic frequencies, as evidenced by the small errors relative to the errors obtained using the RHF method in Table 2. For example, the absolute errors in cc-pV*x*Z CBS estimates of the water harmonic frequencies are 100−298, 19−34, 12−36, and 9−14 cm^{-1} using RHF, B3-LYP, MP2, and CCSD(T), respectively. In contrast, the RHF method apparently yields *more* accurate CBS estimates of the oxygen isotropic shielding than the B3-LYP or MP2 method probably due partly to compensation of errors (e.g., a less-accurate geometry compensating the errors in the GIAO-RHF method) and partly to the lack of MP2 data for the largest cc-pV6Z or pc-4 basis set, resulting in poorer fits.

For a given basis-set family, the MP2 calculations with all electrons correlated, MP2(full), and with core electrons frozen, MP2(FC), show interesting differences. Both pc-*n* and aug-cc-pV*x*Z basis sets lack tight correlation functions, so the MP2(full) calculations may not be correlating the core electrons. Nevertheless, the MP2(full) water properties (O−H bond length, $H\hat{O}H$ bond angle, dipole moment, energy, ω_1 and ω_2 harmonic frequencies, oxygen shielding anisotropy, and hydrogen rovibrationally corrected isotropic shielding) computed with either the pc-*n* or aug-cc-pV*x*Z basis-set family are generally closer to the respective experimental values than the corresponding MP2(FC) numbers. However, the MP2(full) calculations exhibit more pronounced scatter and converge slower than the MP2(FC) calculations (Figure 2c).

NH_3. Because an accurate prediction of nitrogen nuclear shieldings is essential for comparing theoretical and experimental parameters in solid-state and high-resolution NMR studies on metalloproteins (see the introduction), ammonia isotropic shieldings and shielding anisotropies at the RHF and DFT levels have been obtained in the CBS limit and compared with experiment and literature values in Table 4.[66,67] In the CBS limit using the pc-*n* and/or aug-cc-pV*x*Z basis sets, the results in Table 4 show that RHF appears to yield more-accurate NMR parameters than B3-PW91: Although both RHF and B3-PW91 underestimate the measured nitrogen isotropic shielding (σ_N), RHF yields σ_N values in closer agreement with experiment than B3-PW91. Furthermore, RHF could predict the nitrogen shielding anisotropy accurately ($\Delta\sigma_N = 20$ ppm), whereas B3-PW91 overestimate the measured value by ~ 4 ppm. However, both methods yield similar hydrogen isotropic shielding values (31.3−31.5) that are close to the experimental number, 30.7.[68]

TABLE 4: Absolute Isotropic Shielding and Shielding Anisotropy (in ppm) of NH_3 Calculated with the aug-cc−pV*x*Z and pc-*n* Basis Sets in the CBS Limit Using Various Methods[a]

method	basis sets[a]	N_{max}[b]	σ_N	σ_H	$\Delta\sigma_N$	$\Delta\sigma_H$
experiment			264.5 ± 0.05[c]	30.68[d]	20.0[c]	
RHF[e]	aug-cc-pV*x*Z	570	260.73	31.30	20.08	16.26
RHF[e]	pc-*n*	298	260.31	31.32	19.99	16.25
RHF[e]	aug-cc-pV*x*Z*	195	260.52	31.56	20.03	15.75
RHF[e]	pc-*n**	115	261.01	31.67	20.16	15.19
B3-PW91[e]	aug-cc-pV*x*Z	570	259.27	31.44	23.95	15.56
B3−PW91[e]	pc-*n*	298	257.04	31.47	24.22	15.54
B3-PW91[e]	aug-cc-pV*x*Z*	195	258.56	31.73	24.05	15.10
B3-PW91[e]	pc-*n**	115	259.82	31.83	24.03	14.88
CCSD(T)	pz3d2f/pz3p		270.7[f]	31.6[f]	21.9[f]	16.2[f]

[a] An asterisk denotes locally dense basis on N and 6-31G* on H. [b] Maximum number of basis functions in largest aug-cc-pV6Z or pc-4 basis set. [c] From Kukolich, 1975.[66] [d] From Raynes, 1977.[68] [e] Based on the fully optimized B3PW91/6-311++G** geometry. [f] From Gauss and Stanton, 1996[67] based on the experimental geometry.

Using the pc-*n* basis sets instead of the aug-cc-pV*x*Z basis sets reduces the computational effort significantly: For a given theory level, both basis-set families in the CBS limit yield essentially identical N and H isotropic shielding and shielding anisotropies, but the maximum number of basis-set functions is 570 in the aug-cc-pV6Z basis, which is reduced to 298 in the pc-4 basis. Using the locally dense large basis set on N with a smaller 6-31G* basis set on H atoms (denoted by aug-cc-pV*x*Z* or pc-*n**) instead of the unified aug-cc-pV*x*Z or pc-*n* basis sets on both N and H atoms also reduces the computational effort. In the CBS limit, the locally dense basis sets yield NMR parameters that differ by <3 ppm from the respective unified basis sets, but they employ fewer basis-set functions (195 in the aug-cc-pV6Z* and 115 in pc-4*, see Table 4). Hence, the pc-*n** basis sets in the CBS limit in conjunction with an appropriate theory level appear to be an efficient way of computing accurate NMR parameters.

Conclusions

The results herein show that for a given theory level the pc-*n* basis sets yield CBS estimates of molecular and/or spectroscopic parameters for hydrogen, water, and ammonia that are similar to the well-established aug-cc-pV*x*Z basis sets. Notably, although the pc-*n* basis sets were originally designed for RHF and DFT calculations, they could also be used to approach the basis-set limit at correlated MP2 and CCSD(T) levels. In the CBS limit, the theory level rather than the basis-set family dictates the absolute accuracy of a given molecular or spectroscopic property. Thus, using a sufficiently high theory level; for example, CCSDT or CCSDTQ, the pc-*n* basis sets allow accurate predictions of molecular and spectroscopic properties in the CBS limit.

The results herein also show that the pc-*n* basis sets exhibit faster convergence for most structural and/or spectroscopic properties of hydrogen, water, and ammonia than the aug-cc-pV*x*Z ones. This is mainly because the largest pc-4 basis set employs far fewer basis functions than the corresponding aug-cc-pV6Z; that is, 176 versus 254 for hydrogen, 321 versus 443 for water, and 298 versus 570 for ammonia. Further investigations for a larger variety of systems will verify if indeed the pc-*n* basis sets are an efficient means of performing accurate calculations on small- to medium-sized molecular systems, as suggested by the present calculations. Furthermore, they could be used within the locally dense basis-set approximation to estimate accurate molecular or spectroscopic properties, for example, NMR parameters, for larger systems such as the active site of enzymes.[69]

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Supporting Information Available: Convergence patterns for selected molecular and spectroscopic parameters of hydrogen and water. This material is available free of charge via the Internet at http://pubs.acs.org.

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