Gaussian basis sets for use in correlated molecular calculations. VI. Sextuple zeta correlation consistent basis sets for boron through neon

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Abstract

The family of correlation consistent polarized valence basis sets (cc-pVXZ) has been extended to include sextuple zeta sets (cc-pV6Z) for the atoms boron through neon. Potential energy functions have been calculated with these sets for the electronic ground states of N_2 and HF using a number of correlated wave functions: MP2, MP3, MP4, CCSD, CCSD(T) and CAS+1+2. Spectroscopic constants have been calculated for each level of theory and have been compared with experiment. Combining these results with those of prior studies, complete basis set limits have been estimated for E_e, D_e and r_e. It is found that the cc-pV6Z basis sets yield dissociation energies that are within 0.6–0.8 kcal mol^{-1} (N_2) and 0.1 kcal mol^{-1} (HF) of the estimated CBS limits. Adding core-core and core-valence contributions to the CCSD(T) CBS limits yields D_e's that are within 0.1 kcal mol^{-1} of the experimental values.

Keywords: Correlated molecular calculations; Gaussian basis set; Sextuple zeta correlation consistent basis set

1. Introduction

Many methods are available to quantum chemists to account for the effects of electron correlation on the electronic structure of atoms and molecules. These methods include Møller–Plesset perturbation theory techniques (MP2, MP3, MP4), single and multireference configuration interaction methods (CISD and MRCI [1]), and coupled cluster methods [CCSD and CCSD(T)] [2–5]. Unfortunately, nearly all studies employing these methods share one limitation, the use of an incomplete basis set approximation to represent the occupied and virtual orbitals.

Although the use of incomplete basis sets is currently unavoidable for most practical problems, the accuracy of the correlated molecular wave functions is strongly dependent upon the quality of the one-particle basis set used. A highly correlated method combined with a small basis set may provide little information about the accuracy or reliability of the correlation method itself. The inherent accuracy of a correlated electronic structure method can only be assessed if the complete basis set (CBS) limit can be reliably determined. High-accuracy basis sets are thus desirable as they provide estimates of the CBS limits.

Several basis sets that have been developed are capable of yielding very accurate results. Examples are the basis sets based upon atomic natural orbitals (ANO) first proposed by Almlöf and Taylor [6]. However, no systematic studies of the convergence of

these basis sets have been reported. In addition, the ANO sets can become quite expensive in practice because of the large number of primitive functions used to represent the natural orbitals. The primitive sets used in the correlation consistent basis sets (cc-pVXZ, X = D, T, ...) of Dunning and coworkers [7–11] are far more compact than those used in the ANOs. Additionally, the systematic convergence properties of the cc-pVXZ basis sets allows one to estimate the complete basis set limit and, thereby, determine the inherent accuracy of the different correlation methods.

In earlier articles in this series, correlation consistent basis sets were developed through the quintuple zeta (cc-pV5Z) level, including both diffuse sets (aug-cc-pVXZ) and sets designed to describe core-valence effects (cc-pCVXZ). These families of basis sets have been used in a number of benchmark calculations [9–18] to investigate the convergence behavior of the correlation consistent basis sets. It has been found that the correlation energies obtained with the correlation consistent basis sets converge smoothly to apparent complete basis set limits. Many other properties also converge to well-defined limits.

In this work, we extend the correlation consistent series of basis sets to include the correlation consistent sextuple zeta (cc-pV6Z) basis set for the atoms boron through neon. The use of cc-pV6Z basis sets is expected to provide results for atomic and molecular properties that are very near the CBS limit. This, in turn, will make it possible to distinguish between the errors caused by methodology from those caused by the use of an incomplete basis set.

We compute the ground state potential energy functions for HF and N_2 using our new cc-pV6Z basis sets and a range of methods, including CCSD, CCSD(T), MP2, MP3, MP4, and CAS+1+2. Combining these results with those of prior studies [13,15,19], complete basis set limits have been estimated for E_e, D_e and r_e using simple analytical functions. Spectroscopic constants obtained from these calculations include the dissociation energy D_e, equilibrium bond length r_e, fundamental harmonic frequency ω_e, vibrational anharmonicity $\omega_e x_e$, rotational constant B_e, and the vibration-rotation coupling constant α_e.

2. Methodology

2.1. Basis sets

In the development of the cc-pV6Z sets, we followed the prescription given by Dunning [7]. (A similar cc-pV6Z has been reported previously by Bauschlicher and Partridge for nitrogen [20] and carbon [21] and by Feller for oxygen [22]. However, the sets developed in the current article used exactly the same guidelines as the other cc-sets. The BP/cc-pV6Z and F/cc-pV6Z sets were based on slight variations of this process: Bauschlicher and Partridge used a different (sp) set and Feller did not fully optimize the polarization set.) The cc-pV6Z sets consists of (16s10p5d4f3g2h1i) primitive sets contracted to [7s6p5d4f3g2h1i]. The (16s10p) sets were taken from optimized HF atomic calculations and contracted to [7s6p] using the general contraction scheme of Raffenetti [23], with the functions with the smallest exponents being added to the HF atomic orbital set. The polarization functions (d, f, g, h, i) are simple primitive Gaussian functions with exponents that are given by even-tempered expansions,

$$\zeta_i = \alpha\beta^{i-1} \quad i = 1, ..., N_f \tag{1}$$

where N_f is the number of functions in the set. α and β are optimized for each set by minimizing the atomic CISD energy, HF+1+2.

The new correlation consistent sextuple zeta (cc-pV6Z) basis sets are available through the World Wide Web. On the WWW the URL for the order form for the correlation consistent basis sets is: http://www.emsl.pnl.gov:2080/forms/basisform.html.

Follow the instructions on the form to selected the desired basis set(s) and have them e-mailed to you.

2.2. CASSCF + 1 + 2 wave functions

In the CAS calculations on N_2, the active space consisted of all the molecular orbitals arising from the 2s and 2p orbitals of the atoms. This included $2\sigma_g$, $2\sigma_u$, $3\sigma_g$, $3\sigma_u$, $1\pi_{gx}$, $1\pi_{gy}$, $1\pi_{uy}$, and $1\pi_{uy}$ in D_{2h} symmetry. In the CAS calculations on HF, all molecular orbitals arising from the 2s and 2p orbitals of fluorine and the 1s orbital of hydrogen were included in the wave function. This included 2σ-4σ, $1\pi_x$, and $1\pi_y$.

Almlöf et al. [24] and Werner and Knowles [25] have noted in their work on N_2 that at very large internuclear distances, the $2\sigma_g$ and $2\sigma_u$ orbitals mix with the $1\sigma_g$ and $1\sigma_u$ core orbitals. When the core orbitals are not correlated, this results in an artificial raising of the CI energy. As suggested by Peterson et al. [13], we have avoided this mixing effect in both HF and N_2 by using a two-step CASSCF procedure. This allows us to treat all regions of the potential energy curve consistently. In the first step of the procedure, the 1σ and 2σ core were constrained to be doubly occupied in all configurations. The core orbitals were taken from this calculation and used in a second-step, a MCSCF calculation with the full valence active space. For these systems, this procedure does not effect the MCSCF energy. However, it does improve the CI results.

The orbitals obtained from the CAS calculations were used in single and double excitation configuration interaction calculations. For the CASSCF+1+2 wave function, the internally contracted MRCI method of Werner and Knowles [26,27] was used. All of the single and double excitations have been taken with respect to the MCSCF reference. Configurations with two electrons in the external orbital space were internally contracted. Additionally, the frozen core approximation was used.

2.3. Potential energy functions and spectroscopic constants

For both N_2 and HF, potential energy functions (PEF) were calculated using an analytical representation of the computed energy values over the range $-0.3\ a_0 \le (r - r_{expt}) \le + 0.4\ a_0$. Sixth order polynomials in the internal displacement coordinate, $\Delta r = r - r_e$, were used. Spectroscopic constants were determined from the PEF coefficients using the second-order perturbation theory expressions developed by Dunham [28].

The dissociation energies for the CAS+1+2 calculations were obtained using a supermolecule approach, in which the dissociation energy is calculated by subtraction of the diatomic energy at large separation ($r = 50\ a_0$) from the energy of the dimer at the equilibrium separation r_e. For the Hartree–Fock-based correlated wave functions (CCSD, MP2, etc.), the dissociation energies were calculated relative to the energies of the separated atoms.

For the calculations of the atomic energies of $H(^1S)$, $N(^4S)$, and $F(^2P)$, spin-restricted methods were employed. These include the partially spin-restricted coupled cluster method of Knowles et al. [29] and the restricted many-body perturbation theory (MBPT) of Lauderdale et al. [30].

2.4. Electronic structure codes and computers

In this work, we used the MOLPRO 96 suite of ab initio electronic calculations[1], except for the MBPT calculations, which were carried out with the ACES II package.[2] Calculations were performed on the Cray C-90 at NERSC and on IBM RS6000/590's at PNNL.

2.5. Extrapolation to the complete basis set limit

In previous work [12,13,15,31], it was observed that several molecular quantities such as D_e, r_e, and E_e converge to well-defined limits when using the correlation consistent basis sets. This is undoubtedly because of the systematic procedure used to construct the sets. It has been observed that the convergence behavior of these molecular properties is often well described by a simple exponential formula

$$A(X) = A(\infty) + Be^{-CX} \tag{2}$$

where X is the cardinal number of the basis sets ($X = 2$ for cc-pVDZ, $X = 3$ for cc-pVTZ,...). In Eq. (2) $A(\infty)$ represents the estimated complete basis set (CBS) limit for the molecular property A. $A(\infty)$, B, and C, are adjustable parameters which are determined in a nonlinear least squares procedure.

2.6. Counterpoise correction for spectroscopic constants

It is well-known that the counterpoise correction [32] is essential in the calculation of interaction energies for weakly bonded systems. For strongly bound systems, like N_2 and HF, it is generally believed that the basis set superposition error (BSSE) will be very small. Nevertheless, for very accurate calculations BSSE may need to be taken into account. In this study we will investigate the effect of BSSE on the calculated spectroscopic constants of N_2 and HF.

In the limit of a complete basis set, the counterpoise-corrected and uncorrected results should be identical. A point of interest is whether or not BSSE causes erratic behavior in the convergence of the uncorrected results, which, in turn, could have an effect on the estimated CBS limits.

The definition of BSSE of a complex AB most widely employed in the literature is [33]

$$BSSE(R) = E_A^{\{AB\}}(R) + E_B^{\{AB\}}(R) - E_A - E_B \qquad (3)$$

where $E_A^{\{AB\}}$ and $E_B^{\{AB\}}$ are the monomer energies calculated in the complete dimer basis set $\{AB\}$ at a particular AB distance R. We will follow a slightly different definition of BSSE in this article. The BSSE for N_2 at its equilibrium distance will be calculated as the difference of the counterpoise-corrected dissociation energy D_e^{CP} and the uncorrected dissociation energy D_e^{noCP}

$$BSSE(D_e) = D_e^{CP} - D_e^{noCP} = E_{N_2}(r_e^{CP}) - E_{N_2}(r_e^{noCP})$$
$$- 2(E_N^{\{N_2\}} - E_N) \qquad (4)$$

with a similar expression for HF. The last term in Eq. (4) corresponds to the standard definition of BSSE, Eq. (3). The first part of Eq. (4), $E_{N_2}(r_e^{CP}) - E_{N_2}(r_e^{noCP})$, accounts for the fact that the counterpoise corrected equilibrium distance r_e^{noCP} is different than the uncorrected equilibrium distance r_e^{noCP}. Since the equilibrium distances will be similar for the corrected and uncorrected potential energy curves, this term will be very small.

Because the calculation of the monomer energies using the complete dimer basis set increases the computational effort substantially, we will investigate the effects of BSSE just for the CCSD(T) method.

3. Results

3.1. Spectroscopic constants for N_2

The dissociation energy of N_2 has often been used as a test of quantum mechanical methods [13,19,24,25,20]. From experiment, the D_e of N_2 is 228.4 kcal mol^{-1} [34]. Using the SCF procedure provides only about half of the dissociation energy. Thus, treatment of the correlation problem is critical for this molecule. Correlation methods that describe both static (near-degeneracy) and dynamic correlation are required. A complete active space (CAS) wave function can account for static correlation effects; perturbation theory, coupled cluster and configuration interaction techniques are required to describe both effects.

To date, one of the most accurate calculations on N_2 has been done by Almlöf and coworkers [24]. By using an ANO basis set including up through i-functions and performing a multireference configuration interaction (MRCI) calculation, a D_e of 225.0 kcal mol^{-1} was obtained. Werner and Knowles [25] performed CMRCI calculations including i-functions and computed a D_e of 226.7 kcal mol^{-1}. Using a basis set of similar size as cc-pV5Z, they computed the core-core and core-valence correlation contribution to D_e to be 1.29 kcal mol^{-1}. Peterson et al. [13] obtained a directly calculated D_e of 226.3 kcal mol^{-1} using the CAS + 1 + 2 method with a cc-pV5Z basis set. Finally, using a sextuple-zeta basis set that is similar to the present cc-pV6Z set, Bauschlicher and Partridge [20] obtained a D_e of 227.1 kcal mol^{-1}.

The spectroscopic constants calculated in this study plus those previously reported for smaller basis sets by Peterson et al. [13,19] are listed in Table 1. For all correlated methods, the cc-pV6Z set increases the dissociation energy by 0.6 to 1.1 kcal mol^{-1} over the cc-pV5Z results. The largest computed value for D_e, 227.2 kcal mol^{-1}, is obtained from the CAS+1+2 calculation. This differs from experiment by just 1.2 kcal mol^{-1}. CCSD(T) also predicts a very accurate value for D_e, differing from experiment by only 1.4 kcal mol^{-1}. In contrast, Møller–Plesset perturbation theory does not perform well. MP2 and MP4 overshoot the experimental dissociation energy, by 11.2 and 3.1 kcal mol^{-1}, respectively. MP3 is 13.2 kcal mol^{-1} lower than the experimental value.

Table 1
Calculated spectroscopic constants for N_2.[a]

Method	Basis set	E_e (hartrees)	D_e (kcal mol^{-1})	r_e (Å)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	B_e (cm^{-1})	α_e (cm^{-1})
Expt.[b]			228.4	1.0977	2358.6	14.30	1.9982	0.01730
RHF	cc-pVDZ	−108.95556	112.1	1.0773	2758.1	11.20	2.0746	0.01340
	cc-pVTZ	−108.98656	120.4	1.0671	2731.5	10.60	2.1144	0.01360
	cc-pVQZ	−108.99447	121.8	1.0656	2729.5	10.70	2.1204	0.01370
	cc-pV5Z	−108.99619	122.0	1.0654	2730.1	10.80	2.1212	0.01370
	cc-pV6Z	−108.99652	122.2	1.0654	2730.2	10.77	2.1213	0.01372
CCSD	cc-pVDZ	−109.26404	193.6	1.1128	2408.9	13.47	1.9443	0.01586
	cc-pVTZ	−109.35536	208.0	1.0967	2423.8	12.83	2.0018	0.01595
	cc-pVQZ	−109.38427	214.2	1.0931	2435.4	12.76	2.0150	0.01597
	cc-pV5Z	−109.39347	216.3	1.0922	2439.7	12.81	2.0183	0.01601
	cc-pV6Z	−109.39683	217.2	1.0920	2441.2	12.78	2.0193	0.01599
	Est. CBS[c]	−109.3980	217.9	1.0920				
CCSD(T)	cc-pVDZ	−109.27648	200.7	1.1189	2339.1	14.48	1.9231	0.01676
	cc-pVTZ	−109.37394	216.7	1.1038	2346.0	13.86	1.9763	0.01691
	cc-pVQZ	−109.40439	223.1	1.1003	2356.2	13.78	1.9888	0.01693
	cc-pV5Z	−109.41419	225.4	1.0994	2359.8	13.83	1.9919	0.01697
	cc-pV6Z	−109.41778	226.4	1.0992	2361.0	13.80	1.9928	0.01696
	Est. CBS[c]	−109.4189	227.0	1.0992				
MP2	cc-pVDZ	−109.26295	213.4	1.1299	2173.0	20.22	1.8860	0.02083
	cc-pVTZ	−109.35776	229.2	1.1136	2195.3	18.90	1.9414	0.02061
	cc-pVQZ	−109.39022	235.8	1.1104	2204.9	18.67	1.9528	0.02057
	cc-pV5Z	−109.40222	238.4	1.1096	2208.0	18.70	1.9555	0.02060
	cc-pV6Z	−109.40724	239.6	1.1094	2208.6	18.65	1.9562	0.02059
	Est. CBS[c]	−109.4090	240.4	1.1094				
MP3	cc-pVDZ	−109.25616	191.3	1.1051	2529.4	9.66	1.9715	0.01335
	cc-pVTZ	−109.34962	205.8	1.0898	2532.1	9.49	2.0273	0.01366
	cc-pVQZ	−109.37958	212.2	1.0865	2540.2	9.54	2.0397	0.01374
	cc-pV5Z	−109.38905	214.3	1.0856	2543.8	9.61	2.0429	0.01378
	cc-pV6Z	−109.39242	215.2	1.0854	2545.1	9.59	2.0439	0.01378
	Est. CBS[c]	−109.3938	216.0	1.0854				
MP4	cc-pVDZ	−109.28068	203.6	1.1271	2198.9	21.70	1.8953	0.02110
	cc-pVTZ	−109.38034	221.1	1.1134	2191.5	21.20	1.9422	0.02150
	cc-pVQZ	−109.41127	228.0	1.1101	2199.1	21.10	1.9538	0.02160
	cc-pV5Z	−109.42127	230.4	1.1094	2201.1	21.20	1.9563	0.02160
	cc-pV6Z	−109.42490	231.5	1.1092	2201.7	21.13	1.9570	0.02163
	Est. CBS[c]	−109.4260	232.1	1.1091				
CAS + 1 + 2	cc-pVDZ	−109.27094	202.0	1.1196	2328.6	14.81	1.9208	0.01699
	cc-pVTZ	−109.36162	217.9	1.1040	2340.6	14.12	1.9753	0.01708
	cc-pVQZ	−109.38992	224.2	1.1005	2351.6	14.02	1.9880	0.01709
	cc-pV5Z	−109.39895	226.3	1.0996	2355.7	14.06	1.9912	0.01712
	cc-pV6Z	−109.40208	227.2	1.0994	2356.6	14.03	1.9919	0.01711
	Est. CBS[c]	−109.4032	227.8	1.0994				

[a] The results through the cc-pV5Z level are taken from Ref. [12] and Ref. [33]. [b] Taken from Ref. [36]. [c] Estimated CBS limit using Eq. (2). These fits included all sets shown (cc-pVxZ; X = 2,3,4,5,6).

Estimated CBS limits are shown in Table 1 for E_e, D_e, and r_e. The estimated CBS limits determined using correlated methods increase the directly calculated D_e's by 0.6 to 0.8 kcal mol^{-1}. The estimated CBS limit for CCSD(T) is 227.0 kcal mol^{-1} and for CAS+1+2 is 227.8 kcal mol^{-1}.

If the core-core and core-valence correlation contribution obtained by Werner and Knowles [25] is

Table 2
Counterpoise-corrected dissociation energies and spectroscopic constants for N_2 from CCSD(T) calculations

Basis set	D_e (kcal mol^{-1})	r_e (Å)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	B_e (cm^{-1})	α_e (cm^{-1})	BSSE(D_e) (kcal mol^{-1})
cc-pVDZ	195.7	1.1212	2322.7	14.47	1.9153	0.01676	−4.96
cc-pVTZ	214.9	1.1046	2340.2	13.85	1.9732	0.01690	−1.82
cc-pVQZ	222.4	1.1007	2353.3	13.77	1.9874	0.01694	−0.75
cc-pV5Z	225.1	1.0996	2358.6	13.83	1.9912	0.01697	−0.31
cc-pV6Z	226.2	1.0993	2360.4	13.80	1.9924	0.01696	−0.19

added to the estimated CBS dissociation energy for the CAS+1+2 method, the corrected dissociation energy, 229.1 kcal mol^{-1}, overshoots the experimental D_e by 0.7 kcal mol^{-1}. Correcting for the effects of the internal contraction in the MRCI as discussed by Peterson [13] results in an estimated CBS limit for D_e of 228.6 kcal mol^{-1}. This is only 0.2 kcal mol^{-1} higher than the value obtained from experiment. For the CCSD(T) method addition of the core-core and core-valence contributions increases the calculated D_e to 228.3 kcal mol^{-1}, just 0.1 kcal mol^{-1} less than the measured value.

For the equilibrium distance, both the CCSD(T) and CAS+1+2 predictions are in good agreement with experiment. The remaining constants are also well described by both the CCSD(T) and CAS+1+2 methods.

3.2. Counterpoise corrections for N_2

The basis set superposition error (BSSE) is expected to be small for N_2, particularly for the larger basis sets. Almlöf et al. [24] calculated the BSSE for the N_2 dissociation energy to be 0.73 kcal mol^{-1} for a (13s8p6d4f) primitive set contracted to a [6s5p4d3f] ANO basis set. Using a (13s8p6d4f2g1h) primitive set contracted to [6s5p4d3f2g1h], the BSSE correction for D_e was reduced to 0.28 kcal mol^{-1}, which is only 0.1% of the experimental dissociation energy. Since this set is similar in size to the cc-pV5Z basis, the BSSE would not be expected to exceed 0.3 kcal mol^{-1} for either the cc-pV5Z or the cc-pV6Z basis sets.

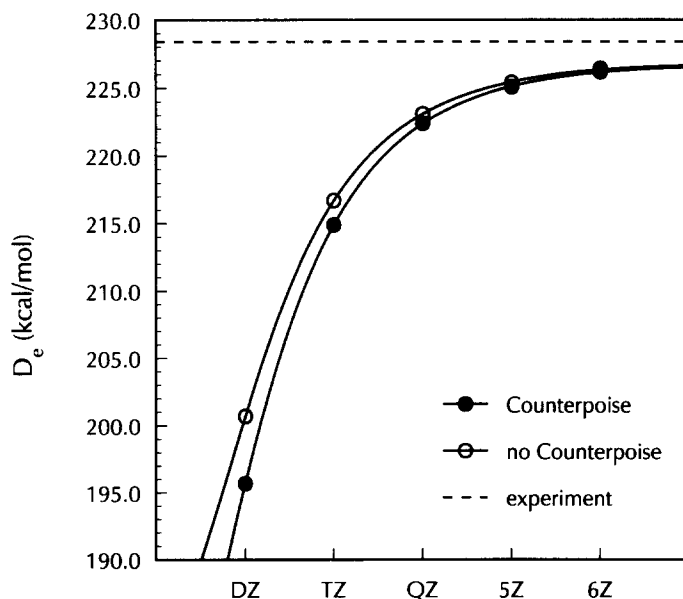The counterpoise-corrected CCSD(T) dissociation energies, spectroscopic constants, and BSSE(D_e) for

Fig. 1. Dissociation energies D_e for N_2 from CCSD(T) calculations with and without the counterpoise correction. The solid lines are fits to Eq. (2).
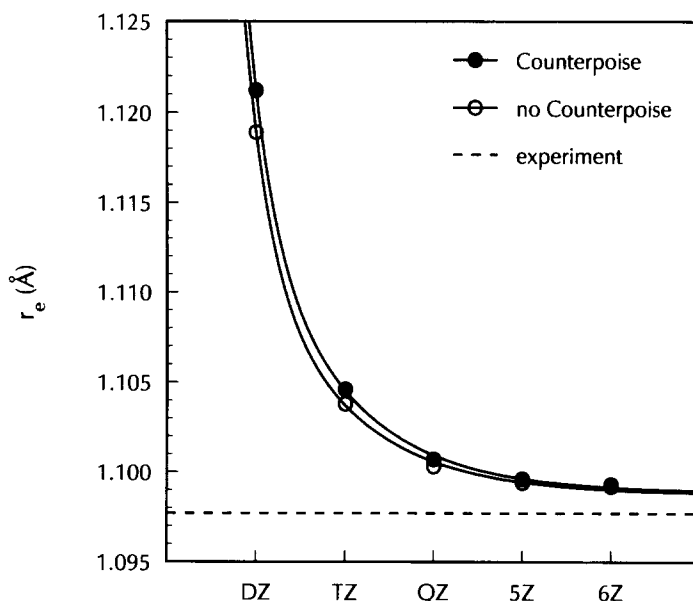
Fig. 2. Equilibrium distances r_e for N_2 from CCSD(T) calculations with and without the counterpoise correction. The solid lines are fits to Eq. (2).

N_2 are shown in Table 2. Figs. 1–3 illustrate the convergence behavior of the corrected and uncorrected D_e, r_e and ω_e, respectively. BSSE is non-negligible for the smaller basis sets (cc-pVDZ and cc-pVTZ), but as shown in the three figures, the counterpoise-corrected and uncorrected results converge smoothly to the same limit for D_e and r_e. As has been observed in previous studies [12,13,15], the harmonic frequencies do not converge regularly. However, the counterpoise-corrected results do
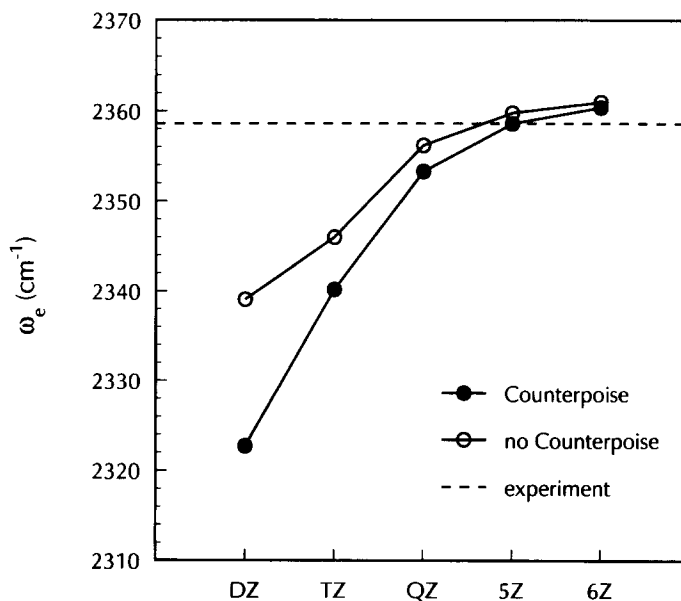

Fig. 3. Fundamental frequencies ω_e for N_2 from CCSD(T) calculations with and without the counterpoise correction.

Table 3
Calculated spectroscopic constants for HF.[a]

Method	Basis set	E_e (hartrees)	D_e (kcal mol^{-1})	r_e (Å)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	B_e (cm^{-1})	α_e (cm^{-1})
Expt.[b]			141.6	0.9168	4138.3	89.90	20.9557	0.79800
RHF	cc-pVDZ	-100.01971	93.2	0.9015	4440.2	85.60	21.6735	0.76420
	cc-pVTZ	-100.05846	99.0	0.8979	4481.1	82.90	21.8476	0.74190
	cc-pVQZ	-100.06818	100.0	0.8969	4476.5	82.90	21.8963	0.74880
	cc-pV5Z	-100.07093	100.3	0.8969	4474.3	83.30	21.8963	0.74900
	cc-pV6Z	-100.07123	100.3	0.8970	4473.3	83.28	21.8912	0.74929
CCSD	cc-pVDZ	-100.22623	125.7	0.9190	4168.6	89.91	20.8581	0.79464
	cc-pVTZ	-100.33199	135.3	0.9152	4211.5	85.58	21.0299	0.76366
	cc-pVQZ	-100.36536	138.1	0.9137	4204.2	86.46	21.0981	0.77743
	cc-pV5Z	-100.37675	139.0	0.9140	4196.7	86.70	21.0842	0.77858
	cc-pV6Z	-100.38049	139.3	0.9142	4193.4	86.67	21.0751	0.77842
	Est. CBS[c]	-100.3820	139.4	0.9139				
CCSD(T)	cc-pVDZ	-100.22816	126.4	0.9199	4149.8	91.10	20.8151	0.80140
	cc-pVTZ	-100.33836	137.0	0.9172	4176.9	86.70	20.9378	0.77040
	cc-pVQZ	-100.37318	140.1	0.9162	4161.7	87.60	20.9835	0.78520
	cc-pV5Z	-100.38518	141.1	0.9168	4150.4	87.90	20.9579	0.78710
	cc-pV6Z	-100.38912	141.4	0.9170	4145.7	87.93	20.9449	0.78715
	Est. CBS[c]	-100.3907	141.5	0.9167				
MP2	cc-pVDZ	-100.22105	129.2	0.9197	4169.6	86.20	20.8264	0.77820
	cc-pVTZ	-100.32979	140.7	0.9180	4178.8	83.80	20.9018	0.75550
	cc-pVQZ	-100.36520	144.1	0.9172	4158.9	85.30	20.9396	0.77310
	cc-pV5Z	-100.37874	145.3	0.9178	4145.7	85.80	20.9118	0.77640
	cc-pV6Z	-100.38374	145.7	0.9181	4140.1	85.91	20.8962	0.77654
	Est. CBS[c]	-100.3854	145.8	0.9177				
MP3	cc-pVDZ	-100.22395	125.0	0.9165	4217.7	87.07	20.9684	0.77819
	cc-pVTZ	-100.33000	134.5	0.9128	4256.5	83.89	21.1397	0.75269
	cc-pVQZ	-100.36372	137.2	0.9113	4247.8	85.10	21.2079	0.76794
	cc-pV5Z	-100.37522	138.1	0.9116	4241.0	85.42	21.1972	0.76934
	cc-pV6Z	-100.37898	138.4	0.9118	4237.7	85.43	21.1884	0.76931
	Est. CBS[c]	-100.3805	138.5	0.9115				
MP4	cc-pVDZ	-100.22816	126.5	0.9197	4156.8	89.50	20.8241	0.79410
	cc-pVTZ	-100.33948	137.8	0.9182	4163.1	86.30	20.8922	0.76990
	cc-pVQZ	-100.37477	141.1	0.9176	4138.7	87.70	20.9196	0.78790
	cc-pV5Z	-100.38701	142.2	0.9184	4122.1	88.40	20.8836	0.79180
	cc-pV6Z	-100.39102	142.6	0.9188	4115.9	88.47	20.8667	0.79249
	Est. CBS[c]	-100.3926	142.7	0.9183				
CAS + 1 + 2	cc-pVDZ	-100.22247	125.3	0.9198	4143.6	92.10	20.8196	0.80780
	cc-pVTZ	-100.32655	134.8	0.9161	4185.6	87.80	20.9881	0.77690
	cc-pVQZ	-100.35917	137.5	0.9146	4179.4	88.60	21.0570	0.79030
	cc-pV5Z	-100.37030	138.4	0.9148	4173.0	88.80	21.0478	0.79130
	cc-pV6Z	-100.37396	138.6	0.9150	4170.2	88.74	21.0396	0.79108
	Est. CBS[c]	-100.3754	138.7	0.9147				

[a] The results through the cc-pV5Z level are taken from Ref. [14]. [b] Taken from Ref. [36] and corrected for relativistic effects. See the text. [c] Estimated CBS limit using Eq. (2). These fits included all sets shown (cc-pVxZ; X = 2,3,4,5,6).

converge smoothly to a well defined limit, though the variation can not be represented by a simple exponential function. The differences between the corrected and uncorrected ω_e gradually decrease as the size of the basis set increases, and appear to approach zero.

3.3. Spectroscopic constants for HF

The calculated spectroscopic constants for HF are collected in Table 3, together with the experimental values and the estimated complete basis set limits. To

properly compare the calculated dissociation energies with the measured value, the effects of spin-orbit splitting must be taken into account. This has been done in the same way as Peterson et al. [15]. One third of the splitting between $J = {}^1/_2$ and $J = {}^3/_2$ states of ^2P atomic fluorine is added to the experimental dissociation energy D_e^{expt} yielding an approximate non-relativistic dissociation energy:

$$D_e = D_e^{expt} + \frac{1}{3}[E(^2P_{1/2}) - E(^2P_{3/2})] \qquad (5)$$

As shown in Table 3, the cc-pV6Z basis set increases the dissociation energy results calculated using the cc-pV5Z set by just 0.2 to 0.4 kcal mol^{-1} for all correlated methods. For all methods, the difference between the CBS limit estimated using Eq. (2) and the results calculated with the cc-pV6Z set is only 0.1 kcal mol^{-1}. This indicates that the cc-pV6Z basis is nearly saturated in both the radial and angular space.

The dissociation energy calculated using the CCSD(T) method with the cc-pV6Z basis set is in excellent agreement with experiment. The calculated D_e is 141.4 kcal mol^{-1}, which can be compared to the experimental value of 141.6 kcal mol^{-1} [35]. MP2 and MP4 overestimate the dissociation energy, by 4.1 and 1.0 kcal mol^{-1}, respectively, while the calculated D_e for MP3 is less than the experimental value by 3.2 kcal mol^{-1}.

The dissociation energy calculated with CAS+1+2/cc-pV6Z differs from the experimental result by 3.0 kcal mol^{-1}. Even at the estimated complete basis set limit the D_e is underestimated by 2.9 kcal mol^{-1}. This was also observed by Peterson et al. [15]. They calculated the spectroscopic constants of HF with the CAS+1+2 method and correlation consistent basis sets up to cc-pV5Z and aug-cc-pV5Z. Their estimated CBS limit is 138.7 kcal mol^{-1} (138.8 kcal mol^{-1} for

the augmented basis sets), which is identical to our estimated CBS limit. Peterson et al. [15] showed that a multi-reference generalization of Davidson's size-extensivity correction [36] for SDCI energies contributes an extra 2.0 kcal mol^{-1} to the aug-cc-pV5Z dissociation energy. We find a similar correction for the cc-pV6Z basis. With the Davidson correction the calculated D_e is 140.6 kcal mol^{-1}, which is 1.0 kcal mol^{-1} smaller than the experimental result.

The CCSD(T) method also yields the best result for r_e. The CCSD(T)/cc-pV6Z value is only 0.0002 Å longer than the experimental value and the estimated CBS limit, calculated with Eq. (2), is just 0.0001 Å shorter than the measured value. The other spectroscopic constants shown in Table 3 do not converge smoothly and no attempt has been made to estimate the CBS limits. However, comparison of the calculated spectroscopic constants with the experimental values reveals that the CCSD(T)/cc-pV6Z results are all very close to the measured values.

3.4. Counterpoise corrections for HF

The basis set superposition error (BSSE) is also expected to be small for HF. The counterpoise-corrected CCSD(T) dissociation energies, spectroscopic constants, and BSSE(D_e) for HF are listed in Table 4. As for N_2, BSSE is substantial for the smaller basis sets, cc-pVDZ (4.0 kcal mol^{-1}) and cc-pVTZ (1.9 kcal mol^{-1}), but decreases to 0.3 kcal mol^{-1} for the cc-pV6Z set.

Previous studies had indicated that the vibrational frequency in HF first increases, then decreases with increasing basis set size. Fig. 4 illustrates the convergence behavior of the BSSE-corrected and uncorrected ω_e's. The counterpoise corrected results show the same general behavior.

Table 4
Counterpoise-corrected dissociation energies and spectroscopic constants for HF from CCSD(T) calculations

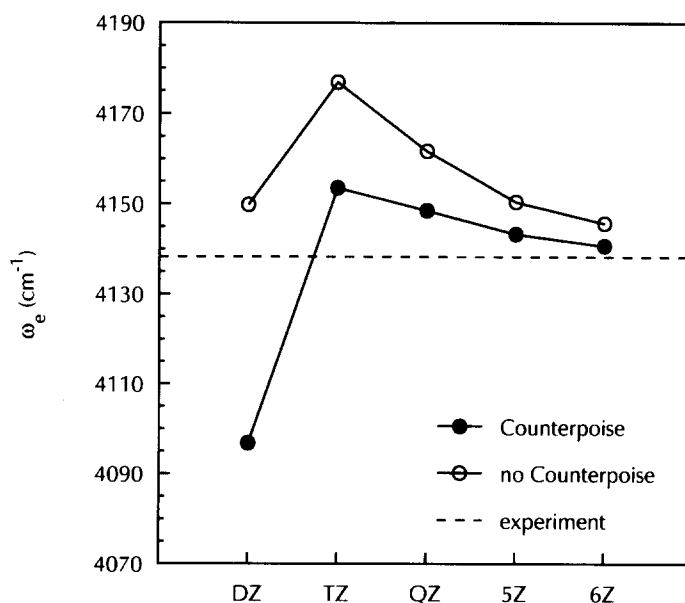| Basis set	D_e (kcal mol^{-1})	r_e (Å)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	B_e (cm^{-1})	α_e (cm^{-1})	BSSE(D_e) (kcal mol^{-1})
cc-pVDZ	122.4	0.9241	4096.8	88.82	20.6277	0.79288	−4.00
cc-pVTZ	135.1	0.9189	4153.5	87.54	20.8563	0.76181	−1.94
cc-pVQZ	139.1	0.9174	4148.5	87.39	20.8588	0.77594	−0.93
cc-PV5Z	140.6	0.9174	4143.3	87.77	20.9292	0.78565	−0.44
cc-pV6Z	141.1	0.9174	4140.7	87.64	20.9274	0.78648	−0.26

Fig. 4. Fundamental frequencies ω_e for HF from CCSD(T) calculations with and without the counterpoise correction.

4. Conclusions

The series of correlation consistent basis sets has been extended to include the sextuple zeta (cc-pV6Z) basis for the first-row atoms boron through neon. Using the correlation consistent basis sets, we have calculated the spectroscopic constants of N_2 and HF for several commonly used methods. These basis sets are among the largest used to date for calculations on N_2 and HF and are expected to yield results close to the complete basis set (CBS) limit.

With the cc-pV6Z basis set the CAS+1+2 dissociation energy of N_2 is calculated to be 227.2 kcal mol^{-1}, 1.2 kcal mol^{-1} less than the experimental dissociation energy (228.4 kcal mol^{-1}). Adding the corrections for extrapolation to the CBS limit (0.6 kcal mol^{-1}), core-core and core-valence correlation (1.3 kcal mol^{-1}), and internal contraction (−0.5 kcal mol^{-1}), the error is reduced to just 0.2 kcal mol^{-1}. CCSD(T)/cc-pV6Z calculations predict a $D_e(N_2)$ of 226.4 kcal mol^{-1}. Adding the correction for extrapolation to the CBS limit (0.6 kcal mol^{-1}) plus that for core-core and core-valence correlation yields a D_e of 228.3 kcal mol^{-1}.

For HF the best results are obtained with the CCSD(T) method. With the cc-pV6Z basis set the HF dissociation energy is calculated to be 141.4 kcal

mol^{-1}, very close to the experimental value of 141.6 kcal mol^{-1}. The equilibrium distance was computed to be 0.9167 Å, only 0.0001 Å shorter than the observed value. In contrast, for HF the CAS+1+2 value for D_e is in error by 3.0 kcal mol^{-1}; the correction for extrapolation is only 0.1 kcal mol^{-1}.

We also investigated the effect of basis set superposition error (BSSE) on the calculated properties of N_2 and HF using the CCSD(T) method. It is found that the counterpoise-corrected and uncorrected results converge to the same limit for both systems. The effect of BSSE on the smaller basis sets, cc-pVDZ and cc-pVTZ, is non-negligible, equaling 5.0 and 1.8 kcal mol^{-1} for N_2 and 4.0 and 1.9 kcal mol^{-1} for HF. The correction decreases to just 0.2 kcal mol^{-1} for the cc-pV6Z sets. In marked contrast to the uncorrected results, it was found that the BSSE-corrected ω_e's for N_2 converged smoothly to a well defined limit, though the variation could not be represented by a simple exponential function. In HF the convergence of ω_e was still somewhat erratic, although the results obtained with the cc-pVTZ through cc-pV6Z sets are much improved by applying the counterpoise correction.

The development of the cc-pV6Z sets for boron through neon brings us one step closer to calculations approaching the complete basis set limit. These sets

should prove to be very useful for highly accurate chemical predictions of properties such as the dissociation energies of small molecules. For larger molecules, using sets of this size is currently unrealistic, though, as the computational machinery continues to improve, it is hoped that sets of these size will become feasible for larger chemical systems.

Acknowledgements

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