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A basis set study of coupled cluster and full configuration interaction calculations of molecular electric properties for BH

Helena Larsen, Christof Hättig, Jeppe Olsen, Poul Jørgensen

Department of Chemistry, University of Aarhus, DK-8000 Århus C, Denmark

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Abstract

Static and frequency-dependent polarizabilities and first and second hyperpolarizabilities have been calculated for BH using full configuration interaction (FCI) and the hierarchy of coupled cluster models CCS, CC2 and CCSD. A systematic basis set investigation has been performed and has been used to estimate basis set limit results. The FCI results are used to calibrate the accuracy of the coupled cluster model hierarchy. No systematic improvements are found in CC2 relative to CCS. The CCSD model appears to be robust and represents a significant improvement relative to CCS and CC2. The CCSD results are in close agreement with the FCI results for α and γ, while for β a similar accuracy requires considerations of a higher level in the coupled cluster hierarchy. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The accuracy of electronic structure calculations for many-electron systems is limited by the form of the N-electron wavefunction and by the choice of the one-electron basis. To make reliable estimates of the errors that are introduced in the one-electron and the N-electron spaces and thus to control the accuracy of a calculation, the approximations in the two spaces must be introduced in a systematic fashion. The ideal approach in ab initio calculations is therefore to employ a well defined hierarchy of wavefunction models and a well defined hierarchy of one-electron basis sets and to explore the hierarchical concept by carrying out a sequence of calculations where the exact solution is approached in a systematic manner.

Full configuration interaction (FCI) calculations give the exact results for the one-electron basis used. FCI results are therefore important for investigating the accuracy of approximate ab initio models because they allow the errors in the wavefunction model to be separated from basis set errors and other effects. Previous FCI benchmark calculations have been used to establish the accuracy of excitation energies in the coupled cluster hierarchy of models CCS, CC2, CCSD and CC3 [10,11].

The importance of FCI benchmark calculations increase with increasing accuracy in the description of the molecular system. This in turn requires that larger and larger basis sets are used. Since there is a factorial growth in the number of determinants with the number of basis functions, FCI benchmark calculations are limited to small molecules and modest basis sets.

In this Letter we present systematic calculations for the ground state polarizability and the first and

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second hyperpolarizabilities of BH. FCI benchmark calculations are carried out and used to monitor the accuracy that is obtained for static and frequency-dependent polarizabilities and hyperpolarizabilities in the coupled cluster hierarchy of models CCS, CC2 and CCSD. CCS and CCSD are the coupled cluster models obtained by truncating the cluster operator after the single and double excitation level, respectively. The CC2 model is obtained from CCSD by approximating the equations that determine the double excitation amplitudes to the lowest non-vanishing order in perturbation theory, whereas the singles equations are unchanged [4]. The computational costs for the coupled cluster models scale as N^4, N^5 and N^6 for CCS, CC2 and CCSD, respectively, where N is the number of basis functions. SCF wavefunction results are used as a reference to investigate the amount of correlation recovered in the coupled cluster calculations.

Some studies of the BH molecule and its polarizabilities and hyperpolarizabilities exist in the literature [3,5,6] but none have been carried out with systematic variations with respect to the basis set. FCI benchmark calculations involving electric properties have previously been described by Kobayashi et al. using a smaller basis [5].

2. Calculational details

The calculations on the BH molecule were carried out for the ground state $X^1\Sigma^+$ at the experimental internuclear distance of 2.3289 a_0 [8] and the 1s orbital was frozen. The series of correlation-consistent basis sets x-aug-cc-pVXZ developed by Dunning and coworkers [1,2,15] were used with varying cardinal number X and augmentation levels x. These basis sets are the most successful of the new hierarchical basis sets and provide an excellent hierarchy of one-electron basis sets consisting of Hartree–Fock atomic orbitals systematically supplemented with correlation functions and with augmented diffuse functions. This enables separate and systematic investigations of the convergence towards basis saturation for the valence and diffuse region, respectively. The coupled cluster and Hartree–Fock calculations were carried out using a local version of the DALTON program [12] with the coupled cluster response code described in Refs. [13,14]. The FCI calculations have been carried out using the LUCIA program [9]. Both programs calculate the cartesian tensor components and from these the isotropic average of the polarizability $\overline{\alpha}$ and the parallel components of the first and the second hyperpolarizabilities have been

Table 1
Static isotropic polarizabilities $\overline{\alpha}(0)$ in au as a function of basis set and wavefunction model

	SCF	CCS	CC2	CCSD	FCI
aug-cc-pVDZ	22.509	24.154	23.081	21.340	21.400
aug-cc-pVTZ	22.738	24.352	23.211	21.627	21.608
aug-cc-pVQZ	22.780	24.379	23.179	21.631	
aug-cc-pV5Z	22.787	24.383	23.165	21.628	
d-aug-cc-pVDZ	22.740	24.384	23.320	21.610	21.618
d-aug-cc-pVTZ	22.786	24.398	23.258	21.662	21.646
d-aug-cc-pVQZ	22.790	24.388	23.198	21.641	
d-aug-cc-pV5Z	22.790	24.386	23.177	21.632	
t-aug-cc-pVDZ	22.758	24.401	23.338	21.626	21.634
t-aug-cc-pVTZ	22.792	24.404	23.263	21.665	21.649
t-aug-cc-pVQZ	22.791	24.389	23.199	21.641	
q-aug-cc-pVDZ	22.761	24.402	23.341	21.628	21.636
q-aug-cc-pVTZ	22.793	24.404	23.263	21.665	
Estimated basis set limit	22.79	24.37 ± 0.02	23.13 ± 0.06	21.62 ± 0.02	21.61 ± 0.04

Table 2
Static hyperpolarizabilities $\beta_{\parallel}(0)$ in au as a function of basis set and wavefunction model

	SCF	CCS	CC2	CCSD	FCI
aug-cc-pVDZ	56.002	36.692	50.564	71.760	76.097
aug-cc-pVTZ	58.084	38.920	46.059	68.238	72.562
aug-cc-pVQZ	56.870	37.310	42.013	64.921	
aug-cc-pV5Z	56.572	36.897	40.567	63.849	
d-aug-cc-pVDZ	58.268	39.273	50.587	71.132	75.120
d-aug-cc-pVTZ	54.866	35.387	42.044	64.398	68.633
d-aug-cc-pVQZ	55.408	35.748	40.704	63.479	
d-aug-cc-pV5Z	55.503	35.809	39.904	62.970	
t-aug-cc-pVDZ	57.175	38.206	49.550	70.382	74.462
t-aug-cc-pVTZ	55.199	35.734	42.365	64.657	68.912
t-aug-cc-pVQZ	55.355	35.688	40.622	63.388	
q-aug-cc-pVDZ	57.148	38.178	49.550	70.405	74.487
q-aug-cc-pVTZ	55.146	35.673	42.284	64.566	
Estimated basis set limit	55.5 ± 0.2	35.7 ± 0.1	39 ± 2	62 ± 1	66 ± 2

calculated. For linear molecules these averages can be calculated as

$$\overline{\alpha} = 1/3(\alpha_{zz} + 2\alpha_{xx}) \quad (1)$$

$$\beta_{\parallel} = 3/5(\beta_{zzz} + 2\beta_{zxx}) \quad (2)$$

$$\gamma_{\parallel} = 1/15(3\gamma_{zzzz} + 8\gamma_{xxxx} + 12\gamma_{zzxx}) \quad (3)$$

with the z axis parallel to the molecular bond axis.

3. Comparison of different wavefunction models

3.1. Static results

In Tables 1–3 we have listed the results of the wavefunction study at the different basis set levels for $\overline{\alpha}$, $\beta_{\parallel}$ and $\gamma_{\parallel}$. The convergence in SCF and in the coupled cluster hierarchy towards the FCI results is nearly independent of the basis sets and the absolute accuracy of the individual wavefunction models can be seen already at the aug-cc-pVDZ basis set level.

Considering the doubly and triply augmented cc-pVTZ results in more detail: In Table 4 the individual components of α, β and γ are given. Especially the differences between the doubly and triply augmented α results are small. For β and γ there is a tendency that the differences for the non-correlated wavefunctions SCF and CCS are similar and differ slightly from the differences for the correlated wavefunctions CCSD and FCI, which are also similar.

The convergence trends in the CCS, CC2 and CCSD series is very similar for α, β and γ. The results show that in general no improvements are obtained from CCS to CC2. For example for β_{zzz} the CCS result, is significantly closer to the FCI result than the CC2 result while the opposite is true

Table 3
Static isotropic hyperpolarizabilities $\gamma_{\parallel}(0)$ in au as a function of basis set and wavefunction model

	SCF	CCS	CC2	CCSD	FCI
aug-cc-pVDZ	7517.1	8856.6	8968.5	8088.9	8165.9
aug-cc-pVTZ	9074.7	10620	10111	9163.8	9274.8
aug-cc-pVQZ	9989.9	11620	10847	9883.1	
aug-cc-pV5Z	10482	12146	11239	10265	
d-aug-cc-pVDZ	10934	12479	12663	11127	11269
d-aug-cc-pVTZ	10840	12522	11940	10701	10862
d-aug-cc-pVQZ	10885	12566	11747	10632	
d-aug-cc-pV5Z	10919	12599	11668	10605	
t-aug-cc-pVDZ	10974	12535	12713	11182	11321
t-aug-cc-pVTZ	10922	12612	12015	10764	10927
t-aug-cc-pVQZ	10906	12587	11763	10642	
q-aug-cc-pVDZ	11163	12726	12911	11378	11516
q-aug-cc-pVTZ	10956	12645	12048	10792	
Estimated basis set limit	10910 ± 40	12590 ± 50	11500 ± 250	10530 ± 130	10730 ± 200

Table 4
Values of the cartesian tensor components calculated using the basis sets d-aug-cc-pVTZ and t-aug-cc-pVTZ and different wavefunction models. The values are given in au

	α_{zz}		α_{xx}		β_{zzz}		β_{zxx}		γ_{zzzz}		γ_{xxxx}		γ_{zzxx}	
	d-aug	t-aug	d-aug	t-aug	d-aug	t-aug	d-aug	t-aug	d-aug	t-aug	d-aug	t-aug	d-aug	t-aug
SCF	22.599	22.600	22.880	22.888	−12.570	−12.191	52.007	52.095	18035	18029	9830.1	9996.8	2487.7	2480.6
CCS	23.357	23.357	24.919	24.927	−23.452	−23.078	41.215	41.317	20710	20706	11322	11497	2926.9	2923.2
CC2	23.173	23.173	23.301	23.308	−34.638	−34.413	52.355	52.511	20482	20460	10815	10958	2594.1	2598.2
CCSD	23.006	23.005	20.990	20.995	−24.076	−23.993	65.703	65.877	18056	18031	9739.8	9852.5	2369.5	2378.8
FCI	23.299	23.298	20.819	20.824	−24.910	−24.813	69.649	69.833	18531	18506	9744.4	9859.5	2449.2	2459.3

for the β_{zxx} component. In general CCSD shows a significant improvement relative to CCS and CC2, both for the individual components of α, β and γ and for $\bar{\alpha}$, $\beta_{\|}$ and $\gamma_{\|}$. The absolute error in CCSD is 0.1%, 6% and 1.5% for $\bar{\alpha}$, $\beta_{\|}$ and $\gamma_{\|}$, respectively. CCSD thus gives accurate results for α and γ, while β is more difficult to describe. The deviation in $\beta_{\|}$ is mainly due to the β_{zxx} component, which differs by about 6% from the FCI results. The difficulties in describing β can be explained by noting that the β components contain two terms. For example

$$\beta_{zzz} = 2\left(\langle 1_z|Z|1_z\rangle - E_1\langle 1_z|1_z\rangle\right) \quad (4)$$

where $|1_z\rangle$ is the first order correction to the wavefunction due to the perturbation Z. In the t-aug-cc-pVTZ basis $\langle 1_z|Z|1_z\rangle = 420.98$ and $E_1\langle 1_z|1_z\rangle = -433.38$. These two terms have the opposite sign. Thus for BH there is an exceptionally large cancellation leading to small β components, which therefore contain large relative errors. The differences between the FCI and the CCSD results indicate that to describe β to the same accuracy as α and γ, the next level CC3 in the coupled cluster hierarchy is required.

The SCF results are closer to the FCI results than the CCS and CC2 results for most of the α, β and γ components with the β_{zzz} component as an exception. Here the SCF result highly overestimates the FCI result. The SCF, CCS, CC2 and FCI results for β_{zzz} are -12.2, -23.1, -34.4 and -24.8 au respectively. For γ the SCF results even seem to have a similar accuracy as the CCSD results. However, this is accidental since it is well known that $\gamma_{\|}$ in most cases has a large dynamical correlation contribution. This conclusion is supported by the frequency-dependent results where, as we shall see below, the SCF wavefunction model does not give better results than the CCS and CC2 models.

3.2. Frequency dependent results

To compare the performance of the SCF and the CCS, CC2 and CCSD wavefunction models with the FCI response approach for the dispersion of the polarizability and the hyperpolarizabilities, we computed with these methods the cartesian tensor components of the polarizability $\alpha(\omega) = \alpha(-\omega;\omega)$, the second harmonic generation $\beta^{\mathrm{SHG}}(\omega) = \beta(-2\omega;\omega,\omega)$ and the third harmonic generation $\gamma^{\mathrm{THG}}(\omega) = \gamma(-3\omega;\omega,\omega,\omega)$. The relative dispersions $\alpha(\omega)/\alpha(0)$, $\beta^{\mathrm{SHG}}(\omega)/\beta(0)$ and $\gamma^{\mathrm{THG}}(\omega)/\gamma(0)$ are given in Table 5 for the d-aug-cc-pVTZ basis. The static components calculated with the same basis set are given in Table 4 as a

Table 5
Relative dispersions $\alpha(\omega)/\alpha(0)$, $\beta^{\mathrm{SHG}}(\omega)/\beta(0)$ and $\gamma^{\mathrm{THG}}(\omega)/\gamma(0)$ calculated using the basis set d-aug-cc-pVTZ

λ (nm)	SCF	CCS	CC2	CCSD	FCI	SCF	CCS	CC2	CCSD	FCI
	α_{zz}					α_{xx}				
1064.0 [a]	1.018	1.018	1.018	1.019	1.019	1.094	1.078	1.079	1.065	1.065
694.3 [a]	1.044	1.043	1.045	1.045	1.046	1.316	1.245	1.248	1.199	1.201
488.0 [a]	1.095	1.093	1.096	1.097	1.100	5.014	2.370	2.471	1.966	2.018
	β_{zzz}					β_{zxx}				
1064.0	1.317	1.225	1.248	1.249	1.255	1.771	1.774	1.620	1.488	1.494
694.3	2.069	1.730	1.787	1.792	1.812	4.444	4.176	3.489	2.815	2.852
488.0	6.779	4.649	4.553	4.551	4.741	169.0	42.61	33.34	16.50	17.51
	γ_{zzzz}					γ_{xxxx}				
1064.0	1.669	1.645	1.661	1.639	1.652	0.371	0.035	0.127	0.067	0.025
694.3	4.743	4.562	4.664	4.384	4.543	2.150	1.998	2.044	1.864	1.883
488.0	9.563	8.784	8.192	3.695	4.191	292.9	78.20	109.6	448.1	216.8

The values are given in au. [a] The corresponding frequencies are 0.042823, 0.065625 and 0.093368 au, respectively.

reference. The results show that the relative dispersion is described with similar accuracy in CCS and CC2. In some cases the CC2 results are a little better and in others cases the CCS results give better predictions. In general it appears that the dispersion is described a little better in CC2 and CCS than in SCF. The CCSD results are in general significantly improved compared to CCS and CC2. Furthermore for all the components, the relative dispersion calculated at the CCSD level is close to the FCI results. Thus the CCSD wavefunction model appears to be robust.

Inspecting the values of the two cartesian tensor components of the second hyperpolarizability some remarkable variations are observed. For γ_{zzzz} the calculated value decreases in CCSD and FCI for the last frequency whereas it increases for the remaining wavefunction models. For γ_{xxxx} the values decrease on going from the static value to the first frequency-dependent value no matter which wavefunction model is employed. Increasing the frequency further leads to an increase in the value of γ_{xxxx}.

To understand this behaviour it should be recognized that $\alpha(\omega)$, $\beta^{\mathrm{SHG}}(\omega)$ and $\gamma^{\mathrm{THG}}(\omega)$ have poles when respectively ω, 2ω and 3ω matches the lowest excitation energy. Koch et al. [10] have calculated the lowest excitation energies for the BH molecule using the cc-pVDZ basis of Dunning augmented with two diffuse functions. The excitation energies do not vary considerably when the basis set is extended. The lowest excitation energy calculated at the CCSD level was 0.1090 E_h for the $A^1\Pi$ state and 0.2359 E_h for the lowest totally symmetric state, $B^1\Sigma^+$. The z-component of the dipole operator for BH is totally symmetric and thus the first pole of $\gamma_{zzzz}(-3\omega;\omega,\omega,\omega)$ is expected for ω at about 0.079 E_h. This pole lies between the last two frequencies at which the hyperpolarizability has been calculated and explains the decrease in the FCI and CCSD results. The large difference between the SCF, CCS and CC2 results on one hand and the CCSD and FCI results on the other indicates how difficult it is to describe what happens in the area around the pole. Furthermore it can be concluded that first at the CCSD level an adequate description is obtained. In a similar way a pole in γ_{xxxx} for $\omega \approx 0.036$ E_h explains the decrease that is observed for the component between the static limit and the first frequency.

4. Basis set investigation

The addition of diffuse functions improves the representation of the outer valence regions of the electronic system, while increasing the cardinal number gives an improved description of the valence region. We will investigate the basis set dependence in the valence and the outer valence region by carrying out two series of basis set investigations for the polarizabilities and hyperpolarizabilities. (1) the x-aug dependence where the cardinal number is fixed and the augmentation level increased and (2) the XZ dependence where the augmentation level is fixed but the cardinal number is increased. Of course, in order to obtain the complete basis set limit, extrapolations in both XZ and x-aug should be made.

Fig. 1(a-b), Fig. 2(a-b) and Fig. 3(a-b) show trends in α, β and γ using the CCSD wavefunctions for the x-aug and XZ functional dependencies.

Let us first consider $\overline{\alpha}$. Inspecting the x-aug plot (Fig. 1a) $\overline{\alpha}$ is seen to increase at all augmentation levels on going from the DZ to the TZ level. At the SCF level it hardly changes when the cardinal is further increased. This is also true for the CCS and CC2 wavefunction models. For CCSD a small decrease is obtained for the polarizability when the cardinal number is increased from TZ to QZ and further to 5Z. The TZ series thus overestimates the polarizability slightly, by less than 1%. At the CCSD levels of theory an acceptable convergence is obtained with the d-aug-cc-pVTZ basis.

The first hyperpolarizability $\beta_{\|}$ does not converge so smoothly as the polarizability. When considering the XZ dependence (Fig. 2b) the variation of $\beta_{\|}$ is seen to be irregular for the aug-cc-pVXZ series. As for $\overline{\alpha}$ two diffuse sets of functions are needed to get a reasonable description. Turning to the x-aug plot (Fig. 2a) the DZ values are seen to converge to a limit that is about 6 au or 9% above the TZ limit. A decrease of 1 au or about 2% is obtained from TZ to QZ and an additional small decrease is obtained from QZ to 5Z.

By comparing the basis set effects of the different wavefunction models, it is seen that for the correlated models CCSD and CC2 $\beta_{\|}$ is reduced when going from the TZ to the QZ series whereas it is about constant for the uncorrelated models CCS and SCF. For the correlated models it thus appears that

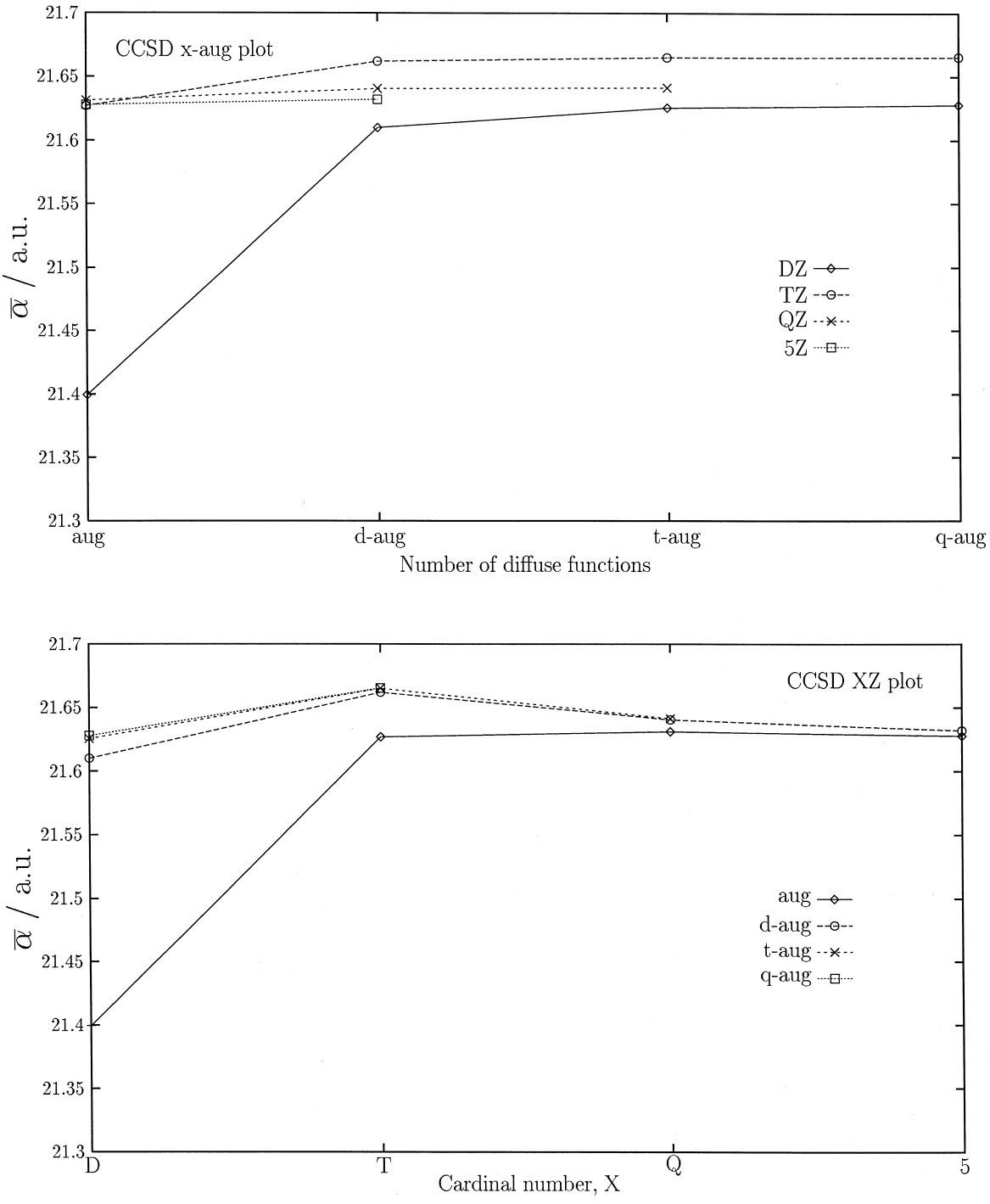


Fig. 1. Behaviour of the dipole polarizability $\overline{\alpha}$ at the CCSD level of theory: (a) x-aug dependence for the x-aug-cc-pVXZ basis sets. (b) XZ dependence for the x-aug-cc-pVXZ basis sets.

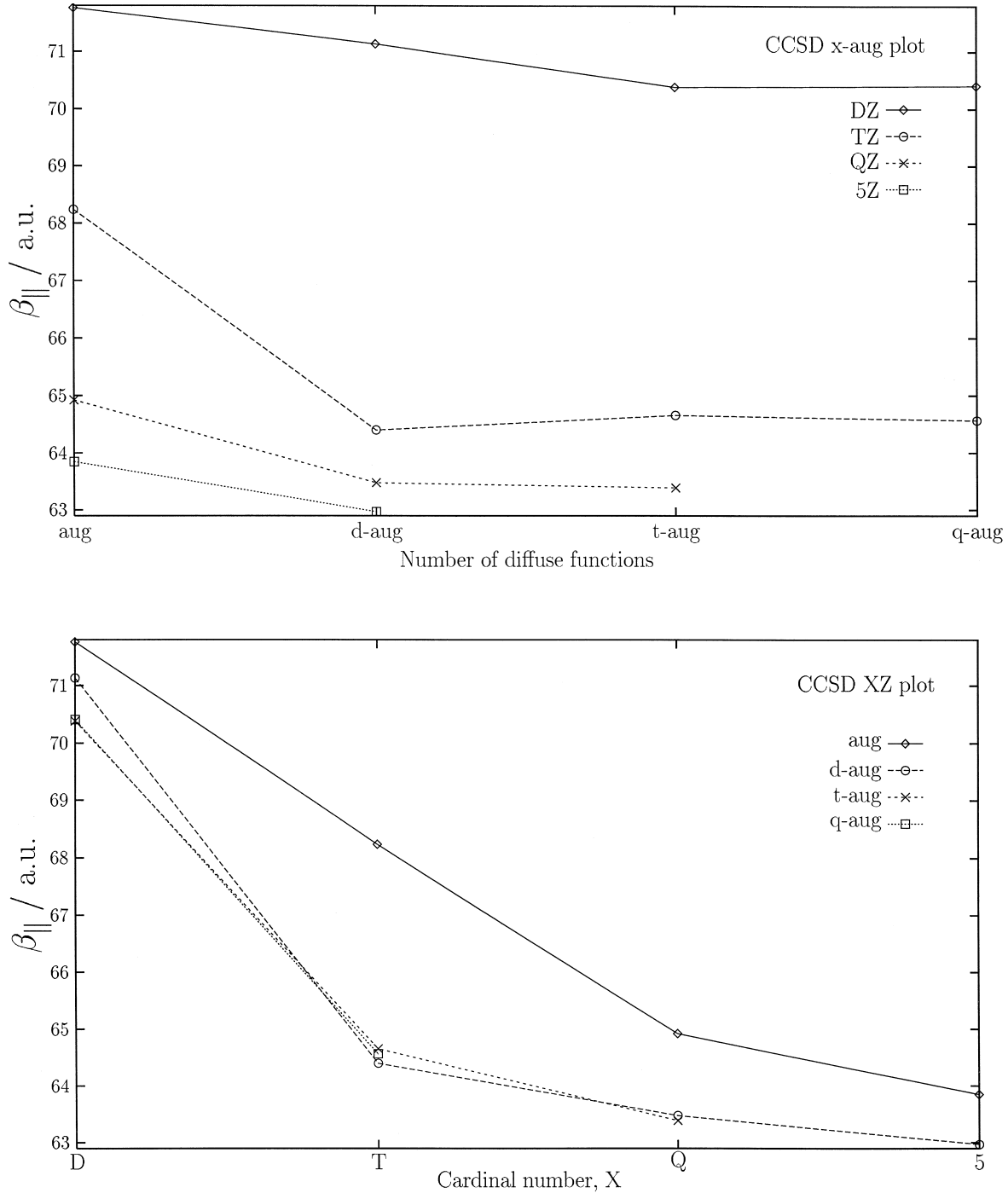


Fig. 2. Behaviour of the first hyperpolarizability $\beta_{\|}$ at the CCSD level of theory: (a) x-aug dependence for the x-aug-cc-pVXZ basis sets. (b) XZ dependence for the x-aug-cc-pVXZ basis sets.

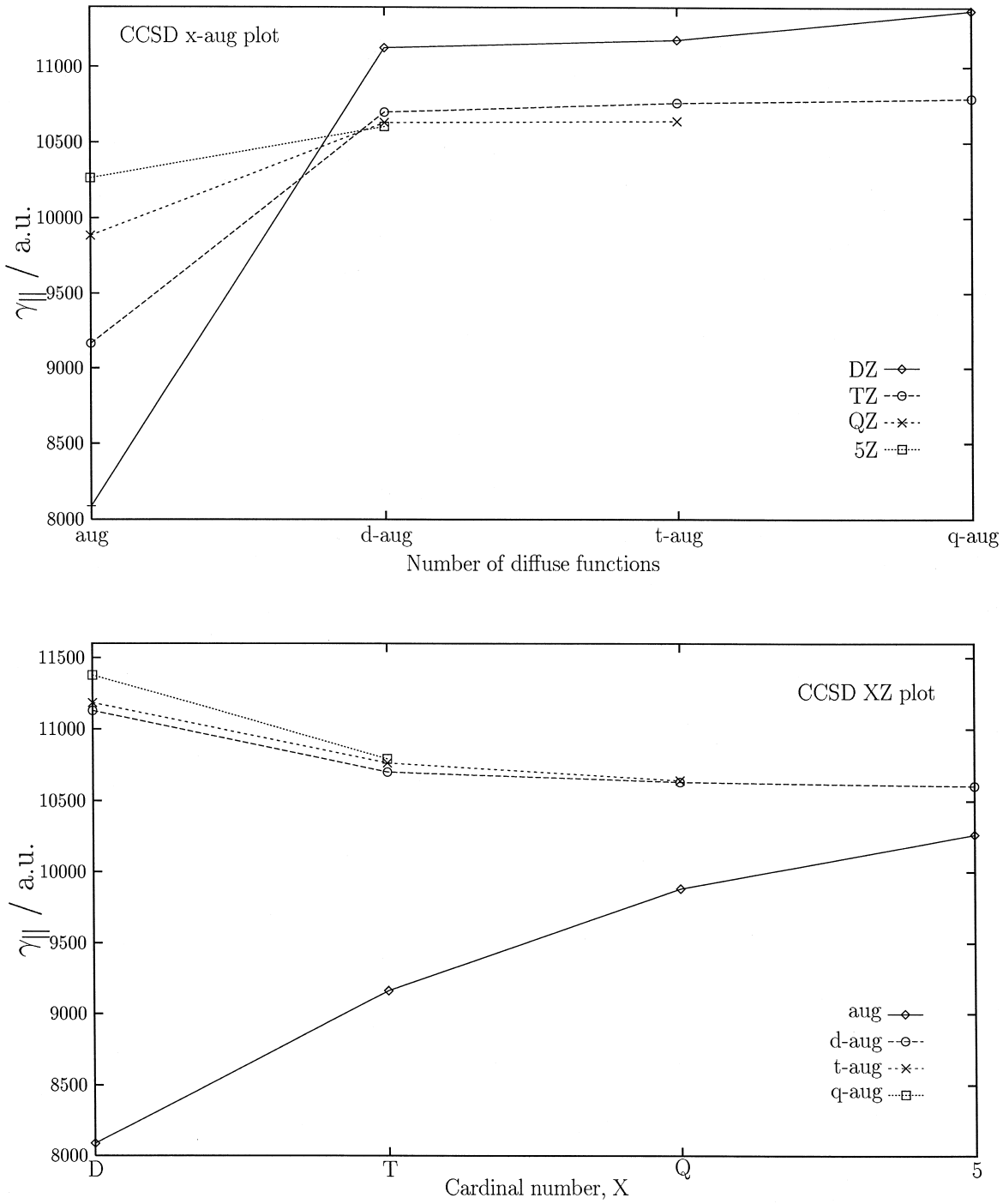


Fig. 3. Behaviour of the second hyperpolarizability $\gamma_{\|}$ at the CCSD level of theory: (a) x-aug dependence for the x-aug-cc-pVXZ basis sets. (b) XZ dependence for the x-aug-cc-pVXZ basis sets.

beyond the double augmentation level it is much more important to increase the cardinal number than to increase the number of diffuse functions.

For $\gamma_{\parallel}$ some of the same trends as for $\beta_{\parallel}$ and $\bar{\alpha}$ are observed. Beyond the d-aug-cc-pVTZ level only small changes are obtained.

In conclusion, it is seen that for both the XZ and x-aug dependence the higher quality basis sets converge rapidly and smoothly toward the basis set limit for both the polarizability and the first and the second hyperpolarizabilities. This is in accordance with the observations of Woon and Dunning [1] for the rare gas atoms. In Tables 1–3 estimated basis set limits for $\bar{\alpha}$, $\beta_{\parallel}$ and $\gamma_{\parallel}$ are given at the bottom line. The estimated basis set limits rely on the fast convergence in the x-aug and XZ series. They have been obtained by taking the t-aug-cc-pVQZ result and adding the differences t-aug-cc-pVQZ - d-aug-cc-pVQZ and t-aug-cc-pVQZ - t-aug-cc-pVTZ with the uncertainty equal to the numerical sum of the added numbers. The shifts obtained by increasing the augmentation level are in general much smaller than the ones obtained by increasing the cardinal number. The latter is the main source of the large uncertainties for $\beta_{\parallel}(0)$.

The CCSD and FCI models are for the larger basis sets seen to have the same convergence trends with respect to saturation of the one-electron basis. Thus an estimated basis set limit for FCI can be obtained by adding the difference between the CCSD value calculated with the t-aug-cc-pVTZ basis set and the basis set limit of the CCSD calculation. The uncertainty is taken to be equal to the added contribution. For $\bar{\alpha}$ and $\gamma_{\parallel}$ this result gives small shifts and thus small uncertainties in the estimated basis set limit for the FCI calculations. For $\beta_{\parallel}$ the shifts are larger and the uncertainty in the estimated FCI results therefore also increased.

Our values agree well with most previous ab initio results. Maroulis and Bishop [6] reported SCF values of 22.71, 55.1 and 12428 au for $\bar{\alpha}$, $\beta_{\parallel}$ and $\gamma_{\parallel}$, respectively. The values for $\bar{\alpha}$ and $\beta_{\parallel}$ are thus in excellent agreement with our extrapolated values while Maroulis and Bishop overestimate the value of $\gamma_{\parallel}$ since no f orbitals were included in their basis. An SCF value for $\bar{\alpha}$ of 22.7 au by Bishop et al. [7] also compares well with our estimate. For $\beta_{\parallel}$ their SCF value of 42.4 au is to small. Again this is expected since the basis set did not include f functions. FCI values where no f functions were employed in the basis set were reported by Kobayashi et al. [5]. Good agreement is obtained for α. The value is 21.29 au. The cartesian component β_{zzz} of -29.25 au is far from our best estimate. The FCI value of the γ_{zzzz} component was also calculated. Considering the basis set used in that calculation their value of 18182 au agrees quite well with our results.

5. Conclusions

Using the cc-pVXZ basis sets of Dunning et al. augmented with diffuse functions calculations have been carried out for the polarizability and the first and second hyperpolarizabilities of BH in full configuration interaction (FCI) and in the hierarchy of coupled cluster models CCS, CC2 and CCSD. The calculations presented are an example of how essential it is to perform FCI benchmark calculations on molecular systems to investigate the performance of approximate models. The accuracy obtained in the benchmark calculations is promising for the future use of the models in the coupled cluster hierarchy. The results show that CCSD is a significant improvement compared to CCS and CC2 both for $\bar{\alpha}(0)$, $\beta_{\parallel}(0)$ and $\gamma_{\parallel}(0)$ and also for their individual components. In general systematic improvements are not seen from CCS to CC2. The SCF results represent in some cases a significant improvement relative to CCS, however exceptions occur as for the β_{zzz} component. The CCSD results for α and γ are in excellent agreement with the FCI results, whereas β requires at least the next level CC3 in the coupled cluster hierarchy for an equally good description.

From the basis set study we have estimated basis set limits for α, β and γ. For the FCI calculations extrapolations to the basis set limit results were obtained based on the CCSD results.

Acknowledgements

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