Polarizabilities and first hyperpolarizabilities of HF, Ne, and BH from full configuration interaction and coupled cluster calculations

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Static and frequency-dependent polarizabilities and first hyperpolarizabilities have been calculated for HF and Ne using full configuration interaction (FCI) and a hierarchy of coupled cluster models: coupled cluster singles (CCS), an approximate coupled cluster singles and doubles model (CC2), coupled cluster singles and doubles (CCSD), an approximate coupled cluster singles, doubles, and triples model (CC3), and coupled cluster singles, doubles, and triples (CCSDT). A previous study of BH concerning FCI benchmarking has been extended to include CC3 and static CCSDT values. Systematic improvements of the polarizabilities and the hyperpolarizabilities are found going from CCS to CCSD and from CCSD to CC3 or CCSDT. Little or no improvement of the polarizabilities and no improvement of the hyperpolarizabilities are seen when going from CCS to CC2. The CCSD results represent a significant improvement over CCS and CC2 but are again surpassed by the CC3 results which agree very well with the FCI values. The relative error for the static polarizability at the CC3 level is 0.11% for Ne and, respectively, 0.16% and 0.20% for α_{xx} and α_{zz} of HF. For β_{zzz} and β_{zxx} the errors are 0.50% and 1.7%, respectively. Only in the challenging case of BH does CCSDT improve the CC3 values. The dispersion for the polarizabilities and hyperpolarizabilities is predicted with increasing accuracy in the CCS–CC2–CCSD–CC3 sequence as expected from the increasing accuracy of the electronic excitation energies. For all molecules the effect of orbital relaxation has been investigated for the static properties. The inclusion of orbital relaxation gives results that are somewhat different from the unrelaxed results but are in general no improvement. © *1999 American Institute of Physics.* [S0021-9606(99)30228-2]

I. INTRODUCTION

Full configuration interaction (FCI) results are important for establishing the accuracy of approximate *ab initio* wave function models. For a given system and a given one-particle basis set, the FCI result is the exact limit for the solution of the electronic Schrödinger equation and is therefore the appropriate benchmark for approximate *ab initio* electronic structure methods. The generality of the conclusions obtained from FCI benchmark studies depends on the ability of the one-particle basis used to provide a physically reasonable description of the molecule and molecular properties that are investigated. However, because of the factorial growth of the number of determinants with the number of basis functions and electrons, FCI benchmarking has typically been limited to systems with few electrons and modest basis sets. Previous FCI studies have also mainly dealt with total energies and only in a few cases with molecular properties because property calculations are computationally more demanding. Due to further development of more efficient FCI algorithms,[1–4] and the constant increase in computing power, FCI calculations on 8–10 electron systems have recently become possible with reasonable basis sets for molecular properties also. In this article we extend previous FCI benchmark studies of total energies for 8–10 electron systems (including Ne and HF)[5–7] to polarizabilities and first hyperpolarizabilities.

We report FCI calculations for static and frequency-dependent polarizabilities of Ne and HF and for the first hyperpolarizabilities of HF. We furthermore examine the accuracy that is obtained for these properties in calculations employing a recently introduced hierarchy of coupled cluster (CC) models consisting of CC singles (CCS), CC2, CC singles and doubles (CCSD), CC3, and CCSD triples (CCSDT).[8,9] This hierarchy of CC models has been designed for accurate calculations of response properties.[8] Previous benchmark studies of excitation energies have shown that at each level the accuracy is improved by roughly a factor of 3.[7,10] Recent investigations of the behavior of the CC hierarchy in computations of static and frequency-dependent polarizabilities and hyperpolarizabilities for BH (Ref. 11) showed that, while no particular improvement was found when going from CCS to CC2, significant improvements were obtained at the CCSD level. We extend this benchmark study on BH (Ref. 11) here to the CC3 and CCSDT models. Furthermore, in Refs. 12–15 polarizabilities and hyperpolarizabilities for several small molecules have been investigated and have given promising results employing the CC hierarchy of models. The results indicate that even though results of mixed accuracy are obtained at the CCS and CC2 levels,

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TABLE I. Ground state total energies (a.u.) and excitation energies (a.u.) from FCI and CC calculations of Ne and HF.[a]

	Ne	HF	Ne	HF	
	E_{tot}	E_{tot}	^1P	$^1\Pi$	$^1\Sigma$
SCF(CCS[a])	−128.496 364	−100.033 466	0.677 53	0.432 22	0.566 72
CC2	−128.705 238	−100.258 260	0.582 64	0.361 07	0.518 13
CCSD	−128.706 807	−100.259 446	0.605 18	0.378 48	0.531 68
CC3	−128.710 043	−100.264 079	0.613 19	0.382 81	0.535 58
FCI	−128.709 869	−100.264 114	0.613 76	0.383 65	0.5373

[a]The ground state total energies in CCS are identical to the SCF total energies.

accurate results can be expected at the CCSD and, in particular, at the CC3 and CCSDT levels.

The performance of the CC3 model for the hyperpolarizability of HF is of particular interest since the CC3 results have been found in a recent investigation to deviate significantly more from the experimental results than the CCSD results.[16] This raised the question as to whether the experimental results were reliable—an issue previously discussed by other authors based on less accurate electronic structure calculations.[17,18] Thus, the present FCI benchmark study may provide further important insight into the performance of the above-mentioned CC methods for the polarizability and hyperpolarizability of HF.

II. COMPUTATIONAL DETAILS

The HF calculations were carried out using the aug-cc-pVDZ[19,20] basis set at an internuclear distance of 1.732 8795 a.u. The direction of the positive z axis is from H to F. For Ne the d-aug-cc-pVDZ basis set was used.[19–21] The BH calculations were performed in accordance with the details described in Ref. 11 with the internuclear distance chosen as 2.3289 a.u. We restrict ourselves here to results obtained using the d-aug-cc-pVTZ basis set. The above basis sets are small enough to make the FCI calculations feasible but still provide reasonable accuracy for the polarizabilities and first hyperpolarizabilities. In the FCI and CC calculations the core electrons were kept frozen in the canonical Hartree-Fock orbitals. In the hyperpolarizability calculations we consider exclusively components of the second harmonic generation hyperpolarizability (SHG) tensor $\beta(-2\omega;\omega,\omega)$.

The FCI calculations have been carried out using the LUCIA program.[22] The orbital relaxed self-consistent field (SCF), Møller-Plesset (MP2), CC2, CCSD, CCSD(T), and CC3 and the orbital unrelaxed CCS, CC2, and CCSD calculations were performed with a local version of the Dalton program.[23] A local version of the ACESII code[24] was used for the CC3 and CCSDT calculations as well as for the calculations of relaxed properties at the CCSDT level. For the unrelaxed CCS, CC2, and CCSD calculations we have used the CC linear and quadratic response implementation described in Refs. 25 and 26, and for the unrelaxed CC3 calculations the implementation of the linear and quadratic response functions reported in Refs. 13 and 16 were employed. The unrelaxed CCSDT results as well as all orbital relaxed results were obtained using finite field methods. For these calculations the β_{zxx} component has been omitted since it was difficult to obtain accurately. Table I reports the total energies obtained in the FCI and CC calculations together with the lowest dipole-allowed excitation energies.

III. RESULTS FROM UNRELAXED CALCULATIONS

A. Polarizabilities of Ne and HF

In Tables II and III we list the FCI polarizabilities of Ne and HF for different frequencies as well as the absolute deviations of the unrelaxed CCS, CC2, CCSD, CC3, and CCSDT results from the FCI values $(\alpha_{\text{model}}-\alpha_{\text{FCI}})$. In Figs. 1–3 the components of the polarizabilities for Ne and HF are plotted as a function of frequency for the various CC models. To emphasize the performance of the CC models we have in Fig. 4 plotted the deviation from FCI for the static polarizability components.

Comparing the performance of the different CC models it is seen that the polarizabilities for Ne and HF are clearly improved when going to higher levels in the CC hierarchy. For both Ne and HF the CCS model underestimates the polarizabilities while CC2, CCSD, CC3, and CCSDT overestimate them. The absolute errors of the CC2 results are somewhat smaller than at the CCS level but of opposite sign. CCSD represents a significant improvement over CCS and CC2, and the CC3 model reduces the absolute error even further by about a factor of 10 for Ne and, depending on the frequency, by a factor of 5–8 for the polarizability components of HF. At the CC3 level the errors of the static results (in comparison with FCI) are 0.11% for Ne, and 0.16% and 0.20% for the α_{xx} and α_{zz} components of HF, respectively. Thus, the CC3 model yields results that are in excellent agreement with the FCI values. The remaining CCSD error is about 1.2% for all three components. For comparison we have included the CCSDT values of the static polarizabilities. For both Ne and HF these values are slightly higher

TABLE II. Polarizabilities (a.u.) of Ne from FCI and CC calculations.

ω/a.u.	0.0	0.1	0.2	0.3	0.4	0.5
FCI	2.673	2.701	2.794	2.974	3.311	4.089
Error						
CCS	−0.233	−0.241	−0.267	−0.322	−0.444	−0.818
CC2	0.150	0.154	0.169	0.202	0.283	0.655
CCSD	0.034	0.035	0.038	0.046	0.065	0.141
CC3	0.003	0.004	0.004	0.005	0.007	0.014
CCSDT	0.006	…	…	…	…	…

TABLE III. Polarizabilities (a.u.) of HF from FCI and CC calculations.

	0.0		0.1		0.2		0.3	
ω/a.u.	α_{xx}	α_{zz}	α_{xx}	α_{zz}	α_{xx}	α_{zz}	α_{xx}	α_{zz}
FCI	4.287	6.210	4.386	6.332	4.759	6.742	6.000[a]	7.625[a]
Error								
CCS	−0.343	−0.324	−0.379	−0.349	−0.531	−0.436	−1.213	−0.647
CC2	0.294	0.426	0.319	0.444	0.440	0.507	1.243	0.663
CCSD	0.052	0.073	0.057	0.076	0.075	0.085	0.190	0.108
CC3	0.006	0.011	0.007	0.011	0.011	0.013	0.034	0.018
CCSDT	0.010	0.016	…	…	…	…	…	…

[a]There is an uncertainty in the last digit due to limited convergence in the solution of the FCI equations.

than for CC3. However, in both cases the deviations from the FCI results are very small, and both CC3 and CCSDT improve the CCSD results significantly.

For the frequency-dependent polarizabilities we note that for all CC models and for all components the relative and absolute errors increase when the poles are approached. For the frequency-dependent results the relative errors at the CC3 level are 0.11%–0.32% for Ne and 0.18%–0.58% and 0.21%–0.27% for α_{xx} and α_{zz} of HF, respectively. At the CCSD level the relative errors are 1.3%–3.4% for Ne and for α_{xx} and α_{zz} of HF they are, respectively, 1.3%–3.2% and 1.2%–1.4%. The relative errors above are given for the range of frequencies listed in Tables II and III, that are 0.1–0.5 a.u. for Ne and 0.1-0.3 a.u. for HF. In Table IV the relative dispersion for the frequency-dependent polarizabilities, $\alpha(\omega)/\alpha(0)$, is given as predicted by the various CC models and FCI. The trends in the dispersion can easily be interpreted in terms of the excitation energies for the lowest lying dipole-allowed electronic transitions included in Table I. The underestimation of the dispersion by CCS is due to the too large excitation energies within this model. The CC2 excitation energies are too small and a too large dispersion is therefore found for the polarizabilities. The excitation energies increase in the CC2–CCSD–CC3 sequence and correspondingly the predicted dispersion decrease systematically towards the FCI results in the same sequence. At the CCSD level the calculated dispersion is within 2.5% of the FCI dispersions, and at the CC3 level the error is reduced further to less than 1%. We note that the frequency interval considered is relatively large and that for typical laser frequencies ($\omega < 0.2$ a.u.) the dispersion at the CCSD and the CC3 levels is correct within 0.4% and 0.1%, respectively. The excellent agreement between FCI and CC3 even quite close to the poles is computationally important since many molecules have lower excitation energies than Ne and HF.

B. First hyperpolarizability of HF

The individual components of the first hyperpolarizability for HF are given in Table V for the various CC models. The FCI numbers have only been calculated for the β_{zzz} component at three different frequencies, and for the β_{zxx} component at zero frequency. In Fig. 5 we have plotted the β_{zzz} component as a function of the frequency. Figure 4 contains a plot of the deviation from FCI for the various CC models for the static β_{zzz} component.

No improvement is obtained when going from CCS to CC2. For β_{zzz} the CCS results are significantly closer to the FCI results than the CC2 results. The CCSD results are again significantly better than the CCS and CC2 values, and the CC3 model reduces the absolute error in the calculated values further by a factor of 5–9. Compared to FCI the relative

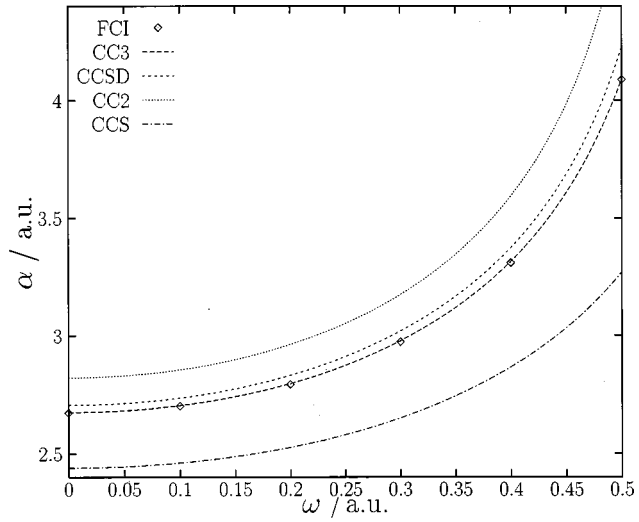


FIG. 1. Polarizability of Ne (a.u.) as a function of frequency (a.u.) in FCI and CC calculations using the d-aug-cc-pVDZ basis set.

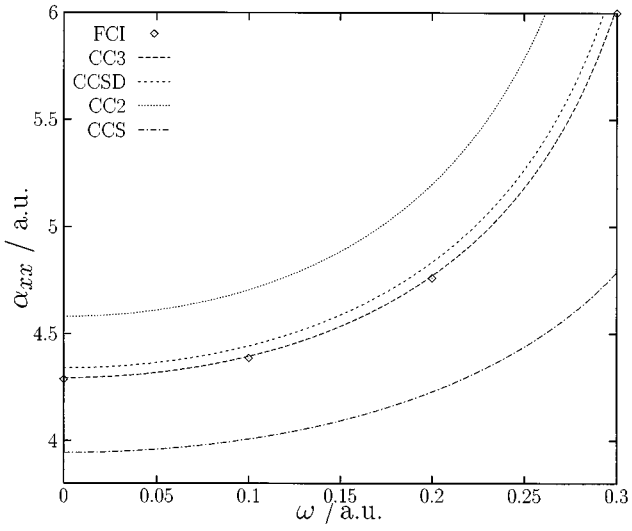


FIG. 2. α_{xx} polarizability of HF (a.u.) as a function of frequency (a.u.) in FCI and CC calculations using the aug-cc-pVDZ basis set.

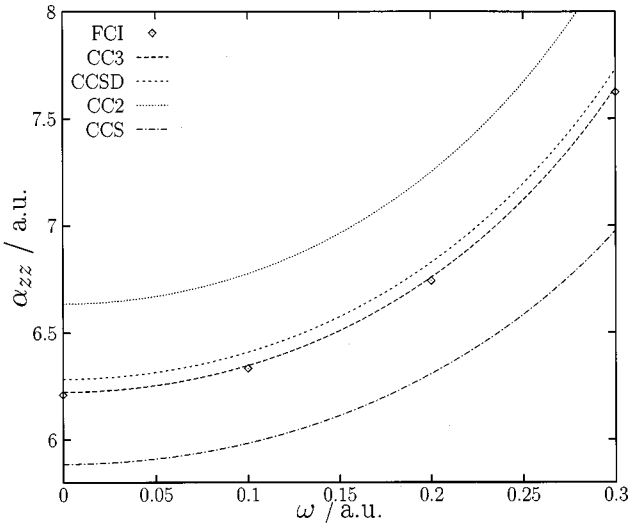


FIG. 3. α_{zz} polarizability of HF (a.u.) as a function of frequency (a.u.) in FCI and CC calculations using the aug-cc-pVDZ basis set.

errors of the CC3 values are 0.50% and 1.7% for the static β_{zzz} and β_{zxx} components, respectively, and at the CCSD level the errors are as high as 4.6% and 10%. These results clearly demonstrate the excellent agreement between CC3 and FCI in the case of hyperpolarizabilities which in general are more difficult to predict than polarizabilities. The difficulties in describing the hyperpolarizability are indicated by the large CCSD relative errors. We have included the CCSDT value for β_{zzz} for comparison, and as for the polarizability the relative error compared to FCI is slightly higher than for CC3 but a significant improvement has been obtained compared to CCSD.

To understand the dispersion of $\beta^{\mathrm{SHG}}(\omega)$, it should be recalled that $\beta^{\mathrm{SHG}}(\omega)$ has poles when either ω or 2ω matches an excitation energy depending on the symmetry of the operators in the investigated component. From the lowest excitation energies in Table I it is seen that the first pole for β_{xxz} is at $\omega \approx 0.19$ a.u. This is in agreement with the change in sign for β_{xxz} observed in the CC3 calculations when going from 0.1 to 0.2 a.u. For β_{zxx} the first pole is at $\omega \approx 0.27$ a.u. However, the β_{zxx} hyperpolarizability changes sign *before* it reaches the first pole and therefore this component also changes from positive at 0.1 a.u. to negative at 0.2 a.u. before going to $-\infty$. It thus has a negative dispersion while the dispersion of β_{xxz} is positive. This is quite interesting since the two components are equivalent in the static case and thus only differ in their dispersion. Also it is a very dramatic breach of the Kleinman symmetry.

To analyze this unusual behavior in more detail we in Fig. 6 have plotted β_{zxx} and β_{xxz} as a function of frequency

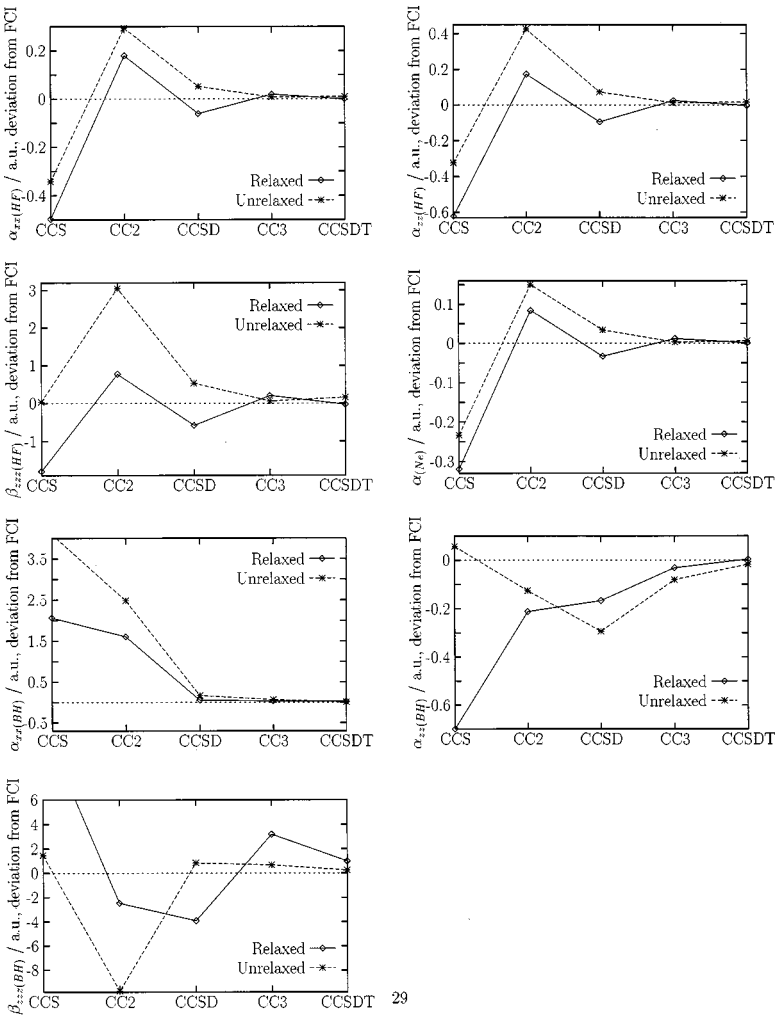


FIG. 4. Deviation from FCI for the unrelaxed and relaxed properties investigated as a function of the coupled cluster wave function model.

TABLE IV. Relative dispersion $[\alpha(\omega)/\alpha(0)$ and $\beta(\omega)/\beta(0)]$ of Ne and HF from FCI and CC calculations.

	α_{xx} (HF)					α_{zz} (HF)				
ω/a.u.	CCS	CC2	CCSD	CC3	FCI	CCS	CC2	CCSD	CC3	FCI
0.1	1.016	1.027	1.024	1.023	1.023	1.017	1.021	1.020	1.020	1.020
0.2	1.072	1.135	1.114	1.111	1.110	1.071	1.093	1.087	1.086	1.086
0.3	1.214	1.581	1.427	1.405	1.400	1.185	1.249	1.231	1.229	1.228
	α (Ne)					β_{zzz} (HF)				
0.1	1.009	1.012	1.011	1.011	1.011	1.153	1.195	1.184	1.186	1.185
0.2	1.036	1.050	1.046	1.045	1.045	2.057	2.569	2.420	2.433	2.425
0.3	1.087	1.125	1.116	1.113	1.113					
0.4	1.175	1.273	1.247	1.240	1.239					
0.5	1.341	1.681	1.563	1.533	1.530					

for the CCSD and CC3 models and separately investigated the different terms that contribute to β_{zxx} and β_{xxz}. In general the first hyperpolarizability is given by

$$\beta^{\mathrm{SHG}}_{ABC}(\omega_A;\omega_B,\omega_C) = P(A,B,C)\sum_{i,j\neq 0}\frac{\langle 0|A|i\rangle\langle i|\bar{B}|j\rangle\langle j|C|0\rangle}{(\omega_A+\omega_i)(\omega_C-\omega_j)}, \quad (1)$$

where A, B, and C are the dipole operators, $\bar{B}=B-\langle 0|B|0\rangle$, $|0\rangle$ is the reference state, and $|i\rangle$ and $|j\rangle$ are excited states. We focus on the contributions from the two lowest lying excited states of $^1\Sigma$ and $^1\Pi$ symmetry. For β_{xxz} the (X,Z,X) term in Eq. (1) is by far the most important in the static and frequency-dependent case. As the pole approaches the $[X(2\omega),Z,X]$ term is more and more dominating ($|i\rangle$ and $|j\rangle$ both equal the $^1\Pi$ state). This $[X(2\omega),Z,X]$ contribution is positive and thus β_{xxz} goes towards ∞. For β_{zxx} the (X,Z,X) term is also leading in the static limit but when going towards the first pole, the $[Z(2\omega),X,X]$ term becomes dominating (in this case $|i\rangle$ equals the $^1\Sigma$ state and $|j\rangle$ the $^1\Pi$ state). This contribution is negative which results in the observed negative dispersion. However, a slight increase in the β_{zxx} dispersion is observed for small frequencies. This must be due to contributions from higher excited states. In our calculations we have only used the aug-cc-pVDZ basis set so one might ask whether we also observe this unusual dispersion behavior with larger basis sets. The same calculations performed with a t-aug-cc-pVTZ basis set gives a maximum further out but eventually β_{zxx} decreases. The contributions due to higher excited states must be bigger and the dominance of the lowest lying $^1\Sigma$ and $^1\Pi$ states is thus postponed.

The first pole for β_{zzz} is around $\omega\approx 0.27$ a.u. As for the polarizabilities the error increases with frequency. However, it should be noted that even close to the poles the CC3 and FCI results are in good agreement. For CC3 the errors relative to FCI are 0.58% and 0.84% for $\beta_{zzz}(\omega=0.1)$ and $\beta_{zzz}(\omega=0.2)$, respectively, and for CCSD 4.4% for both components. The relative dispersion for β_{zzz}, $\beta^{\mathrm{SHG}}_{zzz}(\omega)/\beta_{zzz}(0)$, are given in Table IV. The basic trend is the same as for the polarizabilities. The relative dispersion for $\omega = 0.1$ a.u. at the CCSD and CC3 levels differs by 0.13% and less than 0.1%, respectively, from the relative dispersion found in the FCI calculations.

C. Polarizability and first hyperpolarizability of BH

In a previous study[11] the frequency-dependent polarizabilities and hyperpolarizabilities of BH were investigated in SCF, CCS, CC2, CCSD, and FCI calculations. In Table VI we report the static polarizability and first hyperpolarizability components for FCI together with the absolute errors for the

TABLE V. Hyperpolarizabilities (a.u.) of HF from FCI and CC calculations.

	0.0		0.1			0.2		
ω/a.u.	β_{xxz}	β_{zzz}	β_{xxz}	β_{zxx}	β_{zzz}	β_{xxz}	β_{zxx}	β_{zzz}
CCS	1.061	11.652	1.535	0.984	13.429	17.673	−0.306	23.972
CC2	2.475	14.664	4.858	2.636	17.522	−49.243	0.962	37.670
CCSD	1.706	12.145	3.146	1.713	14.376	−61.646	−0.220	29.397
CC3	1.574	11.673	2.905	1.582	13.846	−73.005	−0.116	28.401
CCSDT		11.774	⋯	⋯	⋯	⋯	⋯	⋯
FCI	1.548	11.614	⋯	⋯	13.766	⋯	⋯	28.164[a]
Error								
CCS	−0.487	0.037			−0.337			−4.193
CC2	0.931	3.050			3.756			9.505
CCSD	0.159	0.531			0.610			1.232
CC3	0.027	0.058			0.080			0.237
CCSDT		0.160						

[a]There is an uncertainty in the last digit due to limited convergence in the solution of the FCI equations.

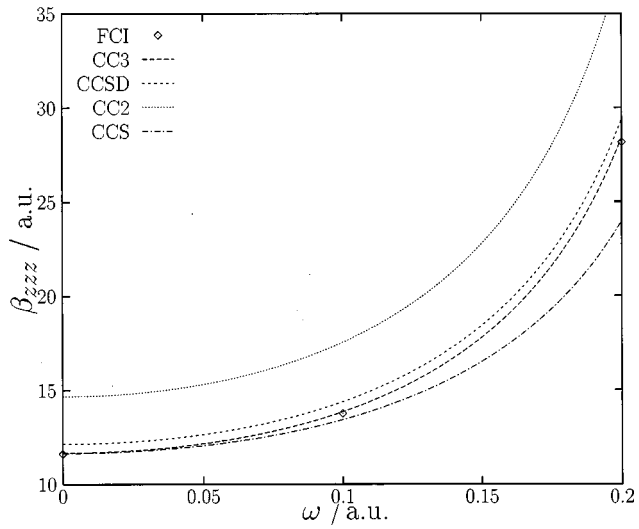


FIG. 5. β_{zzz} hyperpolarizability of HF (a.u.) as a function of frequency (a.u.) in FCI and CC calculations using the aug-cc-pVDZ basis set.

CC wave function models including the CC3 and CCSDT results which were not available in Ref. 11. In addition, we also give results for the β_{xxz} component which were not reported in Ref. 11. Figure 4 also contains a plot of the deviation from FCI for the various CC models for the static α_{xx}, α_{zz}, and β_{zzz}.

For the polarizabilities the relative errors for the CC3 values are 0.32% and 0.34% for α_{xx} and α_{zz}, respectively, which should be compared to the CCSD errors of 0.82% for α_{xx} and 1.26% for α_{zz}, respectively. Thus, for the polarizability of BH CC3 improves the CCSD results although to a smaller extent than for Ne and HF. In this case the CCSDT model improves the values even further to less than a 0.1% error for both α_{xx} and α_{zz}.

In Ref. 11 it was noted that β is very difficult to describe in approximate electronic structure calculations. The relative errors are 3.3% and 5.7% in the case of the CCSD values for β_{zzz} and β_{zxx}, respectively. For $\beta_{\|}$ the error in the CCSD value is 6%. These large relative errors for the components of the first hyperpolarizability of BH were, in Ref. 11, attributed to a large cancellation between contributions of nearly equal size but of opposite sign. In the CC3 calculations the relative errors decrease to 2.7% and 1.5% for β_{zzz} and β_{zxx}, respectively, and to 1.2% for $\beta_{\|}$. Thus, particularly for β_{zxx} the error is significantly reduced when going to the CC3 model in the CC hierarchy. This also results in an improved value for $\beta_{\|}$. As for the polarizability, the improvement at the CC3 level for BH is not as spectacular as for HF, and the CCSDT model improves the results further. For CCSDT the relative error for β_{zzz} is reduced to 1%. However, BH is a notoriously more challenging case with larger correlation effects due to very low-lying excited states. Furthermore, there is the aforementioned problem of the cancellation of terms of similar size but with opposite signs for the hyperpolarizabilities. In light of this the performance of CC3 is good even though the improvement from CCSD to CC3 is more modest in this case than it is for Ne and HF. The CCSDT model here shows better performance as would generally be expected.

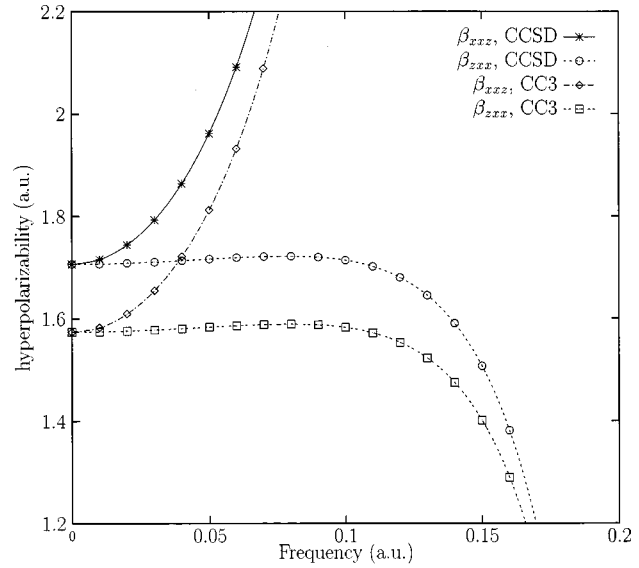


FIG. 6. β_{xxz} and β_{zxx} hyperpolarizabilities of HF (a.u.) as a function of frequency (a.u.) in CCSD and CC3 calculations using the aug-cc-pVDZ basis set.

TABLE VI. Static polarizabilities for BH (a.u.) calculated using the d-aug-cc-pVTZ basis set.

	α_{xx}	α_{zz}	β_{zzz}	β_{zxx}
FCI[a]	20.819	23.299	−24.910	69.649
Error				
CCS[a]	4.100	0.057	1.458	−28.434
CC2[a]	2.482	−0.126	−9.728	−17.293
CCSD[a]	0.171	−0.293	0.833	−3.946
CC3	0.044	−0.102	0.675	−1.045
CCSDT	0.010	−0.017	0.242	

[a]The results are from Ref. 11.

In Table VII the relative dispersion for BH is listed. We will focus solely on the CC3 numbers since the results for the other models have been discussed previously.[11] The calculated CC3 relative dispersion is within 0.1% of the FCI relative dispersion for frequencies not too close to the poles. In Ref. 7 excitations energies of the BH molecule have been calculated using FCI and CC methods using the smaller doubly augmented cc-pVDZ basis. The CC3 excitation energies for the lowest-lying $^1\Sigma^+$ state and the lowest-lying $^1\Pi$ state were within 0.001 a.u. of the FCI results. The CC3 excitation energies for the same states but using the doubly augmented cc-pVTZ basis set used here for the dispersion calculations are 0.2385 a.u. ($^1\Sigma^+$) and 0.1070 a.u.($^1\Pi$). The significantly larger dispersion for α_{xx} in comparison to α_{zz} is therefore not surprising. For α_{xx} (with a pole around 0.107 a.u.) the CC3 dispersion for $\omega=0.093\,368$ a.u. deviates 0.6% from FCI. The β_{zxx} hyperpolarizability has a pole at $\omega=\omega_{1\Pi}\approx 0.107$ a.u. and $\omega=\frac{1}{2}\omega_{1\Sigma}\approx 0.119$ a.u. For β_{zxx} the deviations for $\omega=0.065\,625$ a.u. and $\omega=0.093\,368$ a.u. are 0.6% and 2.2%, respectively. Thus even though the relative dispersion becomes larger for frequencies approaching a resonance, the CC3 model still offers a very good description of the polarizability and hyperpolarizability. This is in agreement with our investigations for HF and Ne.

TABLE VII. Relative dispersion $\alpha(\omega)/\alpha(0)$ and $\beta^{\mathrm{SHG}}(\omega)/\beta(0)$ for BH calculated using the d-aug-cc-pVTZ basis set.

	α_{zz}					α_{xx}				
λ/nm	CCS	CC2	CCSD	CC3	FCI	CCS	CC2	CCSD	CC3	FCI
1064.0[a]	1.018	1.018	1.019	1.019	1.019	1.078	1.079	1.065[b]	1.065	1.065
694.3[a]	1.043	1.045	1.045	1.046	1.046	1.245	1.248	1.199	1.201	1.201
488.0[a]	1.093	1.096	1.097	1.099	1.100	2.370	2.471	1.966	2.003	2.018
	β_{zzz}					β_{zxx}				
1064.0	1.225	1.248	1.249	1.255	1.255	1.774	1.620	1.488	1.491	1.494
694.3	1.730	1.787	1.792	1.814	1.812	4.176	3.489	2.815	2.833	2.852
488.0	4.649	4.553	4.551	4.741	4.741	42.61	33.34	16.50	17.12	17.51
	β_{xxz}									
1064.0	−1.132	−0.087	0.978	1.066	1.110					
694.3	6.125	3.920	2.052	1.849	1.756					
488.0	10.755	6.437	4.122	3.956	3.971					

[a]The corresponding frequencies are 0.042 823, 0.065 625, and 0.093 368 a.u. respectively.

In Table VII we have also included the β_{xxz} component. A comparison with the values for the β_{zxx} component reveals that the difference between the two components increases with frequency. Thus also for BH—although not as spectacular as for HF—a breach of Kleinman symmetry is observed. The first pole for β_{xxz} is at $\omega=\frac{1}{2}\omega_{1\Pi}\approx 0.0535$ a.u. which is in between the two lowest frequencies considered. Accurate prediction of β_{zxx} for the set of frequencies considered is therefore a challenge. While CCS and CC2 fail badly, CCSD and CC3 give more reasonable results.

IV. ORBITAL RELAXED PROPERTIES OF NE, HF, AND BH

In the coupled cluster calculations discussed so far we have used the Hartree-Fock wave function for the unperturbed system as the reference function. Thus, the effects of orbital relaxation have only been treated implicitly by the single excitation part of the cluster operator. Here in Sec. IV we will compare these unrelaxed results to the relaxed CC approach in which the Hartree-Fock orbitals are allowed to relax to the external perturbation.

In Table VIII we have given the static polarizabilities and hyperpolarizabilities using the relaxed SCF, MP2, CC2, CCSD, CCSD(T), CC3, and CCSDT models. For comparison the unrelaxed results are given in parentheses. In comparing the relaxed results it is interesting to note that the CCSD(T) and CCSDT results are in general closer than the CC3 and CCSDT results except for $\beta_{zzz(\mathrm{BH})}$. MP2 is a simpler model than CC2. However, the MP2 values are closer to CCSD than CC2 for Ne and HF. For BH the MP2 and CC2 models give very similar results. In Fig. 4 we have plotted the deviation from FCI for the unrelaxed and relaxed hierarchies for the static (hyper)polarizability components of the three molecules. It should be noted that, since we have employed a frozen core approximation and the 1*s* core orbitals are allowed to relax in the orbital relaxed approach, the FCI

TABLE VIII. Orbital relaxed static polarizabilities and hyperpolarizabilities (a.u.). The unrelaxed values are given in parentheses.

	SCF	MP2	CC2	CCSD	CCSD(T)	CC3	CCSDT	FCI
α_{Ne}	2.353	2.688	2.757	2.640	2.671	2.685	2.674	
			(2.823)	(2.706)		(2.676)	(2.679)	(2.673)
$\alpha_{xx(\mathrm{HF})}$	3.789	4.323	4.467	4.226	4.279	4.306	4.286	
			(4.580)	(4.339)		(4.294)	(4.297)	(4.287)
$\alpha_{zz(\mathrm{HF})}$	5.588	6.201	6.383	6.115	6.199	6.235	6.207	
			(6.636)	(6.283)		(6.223)	(6.226)	(6.210)
$\beta_{zzz(\mathrm{HF})}$	9.820	10.961	12.387	11.034	11.519	11.819	11.587	
			(14.664)	(12.145)		(11.672)	(11.774)	(11.614)
$\beta_{zxx(\mathrm{HF})}$	0.697	1.434	2.153	1.347	1.515	1.651		
			(2.478)	(1.706)		(1.574)		(1.548)
$\alpha_{xx(\mathrm{BH})}$	22.880	22.438	22.425	20.872	20.841	20.854	20.844	
			(23.301)	(20.990)		(20.885)	(20.829)	(20.819)
$\alpha_{zz(\mathrm{BH})}$	22.599	23.081	23.087	23.132	23.281	23.268	23.304	
			(23.173)	(23.006)		(23.219)	(23.282)	(23.299)
$\beta_{zzz(\mathrm{BH})}$	12.591	27.380	28.829	21.735	24.185	23.956	23.927	
			(34.638)	(24.076)		(24.234)	(24.668)	(24.910)

(unrelaxed) and FCI (relaxed) results are not completely identical like they would be if all electrons were correlated.

To estimate the error obtained by comparing FCI (unrelaxed) with the relaxed models we have estimated the total core contribution at the unrelaxed CCSD level as the difference between the values of the properties computed with all electrons correlated and employing a frozen core approximation using the same basis sets as in our other calculations. For Ne and HF the core contributions are very small. The largest core contribution we found is for $\beta_{zzz(\mathrm{HF})}$ where it was 0.005 a.u. For BH a noticeable core contribution is found. For the two components of the polarizability it is 0.05 a.u. whereas for $\beta_{zzz(\mathrm{BH})}$ it is as high as 0.82 a.u. Since the difference between the relaxed and unrelaxed results most likely is significantly smaller than the total core contribution, the relaxation effect of the core can be neglected for Ne and HF but for β_{zzz} of BH, in particular, we may expect the relaxation effects of the core to be rather important.

For Ne and HF the differences between the relaxed and unrelaxed values are very similar. Let us consider the CC2–CCSD–CC3–CCSDT hierarchy. In Ref. 12 a Møller-Plesset order analysis of the relaxed and unrelaxed CC methods was made for the static polarizability. Here it was found that in general the relaxed approach is correct through one order higher than the unrelaxed approach. Thus, relaxed CC2 and unrelaxed CCSD are correct through the same order but CCSD does in general give better results than CC2. Relaxed CCSD is correct through one order higher than unrelaxed CCSD. However, the relaxed approach is only better in some cases, in others the unrelaxed approach gives results closer to that of CCSDT. Both Ne and HF show oscillatory behavior for the deviations from FCI for an increasing level in the CC hierarchy. Note that oscillating but divergent behavior was found for Ne and HF for the Møller-Plesset perturbation series in extended basis sets.[27]

For $\alpha_{xx(\mathrm{BH})}$ the CC hierarchy is seen to converge monotonically towards the FCI result. For $\alpha_{zz(\mathrm{BH})}$ the CCS and CC2 results are unreliable whereas a monotonic convergence is seen for the CCSD–CC3–CCSDT models. Note that monotonic convergence was also found for the Møller-Plesset perturbation series of BH.[27] For α_{xx} and α_{zz} the relaxed approach is a little better than the unrelaxed approach which may be due to the fact that it is correct through one order higher in combination with the monotonically convergent Møller-Plesset series. Because of the large core contribution for β_{zzz} there is a relatively large difference between the CCSDT relaxed and unrelaxed results.

The orbital relaxed and orbital unrelaxed approaches give different numerical results. Nevertheless neither the relaxed nor the unrelaxed approach can be concluded as being preferred over the other for the static properties. The same conclusion was found in previous studies that included more molecules.[12] However, we note that the orbital relaxed properties have poles at the uncorrelated SCF excitation energies. Obviously it is an artifact of a correlated method to have such noncorrelated poles for the frequency-dependent properties. In orbital relaxed approaches the dispersion can thus not be expected to be predicted with similar accuracy as the static properties. This should be kept in mind both for the orbital relaxed iterative CC models (CC2, CCSD, and CC3) as well as for the MP2 and CCSD(T). For the latter two the neglect of orbital relaxation is no option, and the most relevant alternatives to these models for frequency-dependent properties appear to be unrelaxed CC2 and CC3.

V. SUMMARY

In this article we have presented FCI benchmark calculations for HF, Ne, and BH. The performance of the CCS–CC2–CCSD–CC3 hierarchy of CC models has been analyzed for frequency-dependent polarizabilities and first hyperpolarizabilities by a comparison with the FCI results. Rather inaccurate results are generally obtained with the CCS and CC2 models. The CCSD results are generally of high accuracy, although inclusion of triple excitations is required for very accurate results. Considering the computing time and the difficulties in obtaining the CCSDT values numerically the high accuracy that we have seen for the CC3 model is of great importance for future benchmark studies. We have also investigated the effect of orbital relaxation for static properties. Although we can conclude that the orbital relaxed and orbital unrelaxed approaches give quite different results we cannot conclude which one gives consistently better results than the other for *static* properties. The unrelaxed approach is preferable for frequency-dependent properties since the orbital relaxed properties contain an additional set of poles at the values of the SCF excitation energies.

In a recent application of the CC3 method to first hyperpolarizabilities, considerable disagreement with experiment was found for the HF molecule.[16] The very accurate results obtained with the CC3 model in comparison with those of the FCI strongly support the conclusion in Ref. 16 that the source of the disagreement between theory and experiment for HF is either related to a problem in the interpretation of the experimental results or to inaccuracies in the computation of the zero-point vibrational average contribution[17] and/or the pure vibrational contribution.[28] However, the latter contributions are rather small and must be significantly in error (by a factor of 2 or more) in order to explain the discrepancy between theory and experiment.

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