High-order correlation effects on dynamic hyperpolarizabilities and their geometric derivatives: A comparison with density functional results

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Second harmonic generation hyperpolarizabilities and their geometric derivatives have been calculated for HF, HCl, CO, and LiF, using the coupled cluster hierarchies, CCS, CC2, CCSD, CC3, and large correlation-consistent basis sets. The full configuration interaction results have been used to test the accuracy of the coupled cluster results. The CCS and CC2 methods do not improve on the Hartree-Fock results while CCSD is robust and gives significant improvements compared to CCS and CC2. The effects of triples in CC3 are in some cases substantial. Higher order correlation effects are significant for LiF. Including core-valence correlation effects is required only if high accuracy is desired. The coupled cluster results have been used as benchmarks for the results obtained by means of density functional theory using various exchange-correlation functionals. For the hyperpolarizability B3LYP was found to perform best, i.e., to give the results closest to the CC3 ones, while for the geometric derivatives none of the considered functionals was able to give a consistent description for all the considered molecules. © *2006 American Institute of Physics*.
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I. INTRODUCTION

The experimental determination of nonlinear optical properties has attracted a lot of attention during recent years, partly because nonlinear properties are important for the design of new optical materials. The growing experimental interest has been followed by a similarly increasing theoretical interest.[1–14] Among nonlinear optical properties, the frequency-dependent first electric dipole hyperpolarizability takes a prominent place, as it is the simplest third order molecular property, and it is responsible for phenomena such as second harmonic generation[15] (SHG) and Pockel's effect.[15] The geometric derivative of the first hyperpolarizability is also a parameter of interest, because it determines the cross section of hyper-Raman scattering (see, for example, Ref. 16) and contributes to the vibrational part of the hyperpolarizability. In fact, it is the vibrational part, and not the electronic part, which gives in some cases the dominant contribution to the hyperpolarizability.[17,18]

Calculations of nonlinear optical properties for large systems of chemical and technological interests can be performed using density functional theory (DFT).[19–23] However, to establish the accuracy of the DFT results, they must be benchmarked against the results obtained using the hierarchical *ab initio* wave function methods. The present work is aimed in this direction.

In a previous work, one of the authors[24] calculated the dynamic hyperpolarizability and its geometrical derivatives at the coupled cluster singles and doubles (CCSD) level for four diatomic molecules, HF, HCl, LiF, and CO, and used the results to benchmark the DFT results. However, since triple excitation corrections are substantial for dipole polarizabilities,[25–27] and even more for their geometric derivatives,[25] it is important to investigate the effect of triples for hyperpolarizabilities and, in particular, for their geometrical derivatives.

The effect of triples has been investigated in the literature using the approximate iterative triples model CC3 (Refs. 28 and 29) for the first hyperpolarizabilities of HF,[1,23] HCl,[13] CO, and H_2O,[8,23] and for the second hyperpolarizabilities of Ne,[30] Ar, Kr,[31] and N_2.[32] We refer also to the recent review on this subject.[14] When large correlation-consistent basis sets are used, CC3 gives an accuracy comparable to the experimental one. Triple and higher excitation effects on the geometric derivative of the hyperpolarizability have not yet been investigated, and this is the main object of this work. For completeness, we also report the results for hyperpolarizabilities of HF, HCl, and CO, although the CC3 results for them are already available in the literature,[1,13,23] and the present study does not improve on these values. Whenever possible, we have also performed full configuration interac-

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tion (FCI) calculations or CCSDTQ calculations to test the accuracy of the CC3 results. The core correlation effect has also been investigated for the hyperpolarizability and its geometric derivative. Finally, DFT calculations have been performed and benchmarked against *ab initio* results. A somewhat similar study has been performed by Sałek *et al.*,[23] although the set of molecules was different (HF, CO, H_2O, and paranitroaniline), a smaller number of exchange-correlation functionals were studied, and geometric derivatives were not discussed.

The paper is organized as follows. In the next section computational details are given. In Sec. III the convergence of the correlation-consistent basis sets is briefly recapitulated, and after that a study of convergence of the dynamic first hyperpolarizabilities and their geometric derivatives in the coupled cluster hierarchy is reported, with focus on the effect of triples as included in the CC3 model, and on comparison with the FCI results. Next, the core correlation effects are discussed. The obtained results are then used to obtain the best estimate of the hyperpolarizabilities and their geometric derivatives, and these estimates are then used as benchmarks for the DFT calculations with various exchange-correlation functionals. Concluding remarks are given in Sec. IV.

II. COMPUTATIONAL DETAILS

The dynamic hyperpolarizability tensors have been calculated using the coupled cluster hierarchies CCS, CC2, CCSD, and CC3 and, for comparison, using the Hartree-Fock self-consistent field method (HF-SCF). The second harmonic generation hyperpolarizabilities $\beta(-2\omega;\omega,\omega)$ have been calculated for optical frequencies corresponding to wavelengths of 514.5 nm, 694.3 nm, and for infinite wavelength (that is, for the frequencies of 0.088 559, 0.065 625 a.u., and 0 a.u., respectively). Furthermore, FCI calculations have been carried out for static hyperpolarizabilities of HF, HCl, and LiF. For LiF and CO, the β_{zzz} component has been additionally calculated numerically from coupled cluster calculations with full connected triple (CCSDT) and quadruple excitations (CCSDTQ) employing the finite field approach. The accuracy of the numerical differentiation used for the latter two methods was tested for CCSD and found to be better than 0.01 a.u. for β_{zzz}. For all the molecules, in the calculations of the hyperpolarizabilities the z axis was chosen as the main rotation axis and it was pointing from the heavier nucleus to the lighter one.

The geometric derivatives of the hyperpolarizability have been calculated using a numerical three-point centered formula, with a bond length step of 0.001 Å. The following equilibrium geometries were used: 1.128 32 Å for CO, 0.917 Å for HF, 1.2746 Å for HCl, and 1.563 864 Å for LiF.

All SCF, density functional, and coupled cluster calculations were carried out with the DALTON program,[33] while the FCI, CCSDT, and CCSDTQ calculations used the LUCIA code.[34] The implementation of the analytic first hyperpolarizabilities for CCS, CC2, and CCSD has been described by Hättig *et al.*[4] The CC3 hyperpolarizabilities have been obtained from a recent implementation[35,36] in the coupled cluster module[28,29] of the DALTON package.[33] The results are identical with those obtained with the implementation described in Refs. 1 and 27. The orbitals were not allowed to relax in the CC response calculations. Unless explicitly noted, all presented CC results have been obtained using the frozen core approximation. (The 1s orbitals of Li, C, O, and F, and the 1s, 2s, and 2p orbitals of Cl were excluded from the correlation treatment.) The validity of this approximation was investigated by comparing frozen core and all-electron CCSD results. Density functional results obtained by means of local density approximation (LDA),[37,38] BLYP,[39,40] and B3LYP (Refs. 39 and 40) exchange-correlation functionals also used in Ref. 24 have been augmented here by the results calculated using B3P86,[39,41,42] BP86,[39,41] BPW91,[39,43] OLYP,[44] PBE0,[45,46] and PBE (Ref. 45) functionals.

The augmented, doubly augmented and triply augmented correlation-consistent basis sets of Dunning and coworkers[47–50] and Woon[51] have been used throughout this work. The d-aug-cc-pCVTZ set has been used for the all-electron calculations. The FCI calculations have been carried out using the aug-cc-pVDZ basis set for HF and HCl, resulting in 2.48×10^8 determinants. In the case of LiF, a modified aug-cc-pVDZ basis set was employed, in which the diffuse d functions (with 0.0725 exponent for Li and 0.464 exponent for F) were deleted; this basis is occasionally denoted in the text as aug'-cc-pVDZ. This leads to a configuration space of 5.38×10^8 determinants. In the case of the finite field CCSDT and CCSDTQ calculations, the d-aug-cc-pVDZ basis was used for LiF, and the aug-cc-pVDZ basis for CO. For the CC3 and DFT calculations, the t-aug-cc-pVTZ basis set was used.

III. RESULTS AND DISCUSSION

The main focus of this section is to establish how accurately we can evaluate $\boldsymbol{\beta}$ and $\boldsymbol{\beta}'$ (i.e., the first geometric derivative of $\boldsymbol{\beta}$) for HF, HCl, CO, and LiF, using the coupled cluster hierarchy and density functional theory with various DFT functionals. To this purpose, we summarize in Sec. III A the results of a previous CCSD basis set investigation in Ref. 24 and give in addition the results for cardinal number $X=5,6$ for the doubly augmented basis set in order to estimate the CCSD basis set limits. In Sec. III B we report the FCI calculations for smaller basis sets to benchmark the accuracy obtained using the coupled cluster models CCS, CC2, CCSD, and CC3. We also report the calculations performed using the coupled cluster hierarchy and larger basis sets, to further investigate the convergence pattern of the hierarchy. The size of core effects is examined in Sec. III C. In Sec. III D we estimate the correlation/basis set limit results for $\boldsymbol{\beta}$ and $\boldsymbol{\beta}'$ based on the results from the preceding sections, and compare our results with the experimental results for $\boldsymbol{\beta}$. Furthermore, we use our best estimates for $\boldsymbol{\beta}$ and $\boldsymbol{\beta}'$ to benchmark the accuracy of the results obtained using various DFT functionals.

A. Basis set convergence

In Ref. 24 a CCSD basis set investigation has been reported for $\boldsymbol{\beta}$ and $\boldsymbol{\beta}'$ using singly, doubly, and triply aug-

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TABLE I. Basis set convergence of the electronic contributions to β_{xxz}, β_{zzz}, β'_{xxz}, and β'_{zzz} of HF molecule calculated at the CCSD/*n*-aug-cc-pV*X*Z level. All numbers in a.u.

HF Basis	$\boldsymbol{\beta}$		$\boldsymbol{\beta}'$	
	xxz	*zzz*	*xxz*	*zzz*
d-aug-cc-pVDZ	−0.69	−8.64	0.44	−44.90
d-aug-cc-pVTZ	−1.52	−9.77	−0.06	−43.28
d-aug-cc-pVQZ	−1.58	−9.78	−0.49	−42.60
d-aug-cc-pV5Z	−1.60	−9.80	−0.51	−42.83
t-aug-cc-pVDZ	−0.78	−8.93	0.79	−44.16
t-aug-cc-pVTZ	−1.70	−9.86	−0.26	−43.17
t-aug-cc-pVQZ	−1.68	−9.79	−0.51	−42.74

TABLE III. Basis set convergence of the electronic contributions to β_{xxz}, β_{zzz}, β'_{xxz}, and β'_{zzz} of CO molecule calculated at the CCSD/*n*-aug-cc-pV*X*Z level. All numbers in a.u.

CO Basis	$\boldsymbol{\beta}$		$\boldsymbol{\beta}'$	
	xxz	*zzz*	*xxz*	*zzz*
d-aug-cc-pVDZ	7.49	29.65	−8.31	−11.56
d-aug-cc-pVTZ	7.01	28.36	−6.96	−8.36
d-aug-cc-pVQZ	6.71	28.40	−7.44	−7.32
d-aug-cc-pV5Z	6.64	28.35	−7.53	−7.22
t-aug-cc-pVDZ	7.40	29.82	−8.20	−9.14
t-aug-cc-pVTZ	6.81	28.46	−7.53	−7.89
t-aug-cc-pVQZ	6.69	28.36	−7.58	−7.61

mented basis sets and cardinal numbers $X=D,T,Q$. As seen from Figs. 1–4 in Ref. 24, the aug-cc-pV*X*Z series converges very slowly towards the basis set limit, in line with other observations,[8,13,14] emphasizing that single augmentation is insufficient to assure fast convergence for nonlinear properties. With the double and triple augmentations the convergence is faster. The convergence with respect to the cardinal number X is slow and in general even slower for the components of the $\boldsymbol{\beta}'$ tensor than for the components of the $\boldsymbol{\beta}$ tensor (see Figs. 1–4 in Ref. 24). To estimate the CCSD basis set limit, we have carried out calculations of static $\boldsymbol{\beta}$ and $\boldsymbol{\beta}'$ for HF, HCl, and CO using doubly augmented basis sets and cardinal number $X=5$. For HCl we have further carried out calculations for cardinal number $X=6$. The doubly and triply augmented basis set results are given in Tables I–IV.

The results from Tables I–IV show that basis set convergence is approached at the $X=5$ level: the differences between d-aug-cc-pV5Z and d-aug-cc-pV6Z for HCl are below 1% for all properties except for β_{xxz}, which has a very small absolute value. For Li, augmented basis sets with higher cardinal number than $X=Q$ do not exist, so the largest basis set we have been able to use for LiF is t-aug-cc-pVQZ. For HF, HCl, and CO the t-aug-cc-pVQZ results are reasonably close to those obtained with larger basis sets, so the error introduced by using only t-aug-cc-pVQZ for LiF should not be very large, either. The t-aug-cc-pVTZ basis set, used for subsequent CC3 calculations, yields the results which are far from converged, (see especially the β'_{xxz} component of HF), but CC3 calculations with a much larger basis sets would be too resource consuming to be feasible.

TABLE II. Basis set convergence of the electronic contributions to β_{xxz}, β_{zzz}, β'_{xxz}, and β'_{zzz} of HCl molecule calculated at the CCSD/*n*-aug-cc-pV*X*Z level. All numbers in a.u.

HCl Basis	$\boldsymbol{\beta}$		$\boldsymbol{\beta}'$	
	xxz	*zzz*	*xxz*	*zzz*
d-aug-cc-pVDZ	0.24	−17.42	20.20	−38.66
d-aug-cc-pVTZ	−1.16	−12.74	17.43	−38.78
d-aug-cc-pVQZ	−0.80	−12.28	16.45	−39.24
d-aug-cc-pV5Z	−0.84	−12.20	16.34	−39.33
d-aug-cc-pV6Z	−0.80	−12.12	16.30	−39.39
t-aug-cc-pVDZ	0.66	−17.71	19.96	−39.91
t-aug-cc-pVTZ	−0.93	−12.84	17.22	−38.16
t-aug-cc-pVQZ	−0.80	−12.27	16.63	−39.21

B. Coupled cluster hierarchy

The convergence of the calculated hyperpolarizabilities and their geometric derivatives in the coupled cluster hierarchy is first discussed in terms of comparison of the static CCSD and CC3 results to the FCI (or CCSDTQ in the case of CO) results obtained for small basis sets. After that, the performance of the CCS-CC3 series is considered for dynamic hyperpolarizabilities and their geometric derivatives using larger basis sets.

For the molecules HF and HCl, the accuracy of the coupled cluster models is established from comparison with the FCI results using the aug-cc-pVDZ basis set. The results are summarized in Table V. In the case of HF, the FCI results are identical with those of Ref. 5. In general, there are substantial differences between the results obtained using the small basis sets in Table V and the near basis set limit results in Tables I and II. However, in all cases the signs of $\boldsymbol{\beta}$ and $\boldsymbol{\beta}'$ and the ratio β_{xxz}/β_{zzz} are qualitatively correct. We therefore expect that the basis set is large enough to describe the major part of the correlation, and yet small enough for the FCI calculations to be feasible.

The results in Table V show that the CC3 results for HF and HCl are very close to the FCI limit: we find the relative FCI-CC3 differences to be below 1% in most cases. The relative deviations are large only for cases with rather small

TABLE IV. Basis set convergence of the electronic contributions to β_{xxz}, β_{zzz}, β'_{xxz}, and β'_{zzz} of LiF molecule calculated at the CCSD/*n*-aug-cc-pV*X*Z level. All numbers in a.u.

LiF Basis	$\boldsymbol{\beta}$		$\boldsymbol{\beta}'$	
	xxz	*zzz*	*xxz*	*zzz*
d-aug-cc-pVDZ	40.11	33.90	51.58	94.17
d-aug-cc-pVTZ	29.65	29.68	50.42	80.05
d-aug-cc-pVQZ	28.38	28.12	47.09	76.24
t-aug-cc-pVDZ	35.90	31.80	51.69	92.13
t-aug-cc-pVTZ	29.70	29.82	50.12	80.44
t-aug-cc-pVQZ	28.37	28.42	47.22	76.54

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TABLE V. Comparison of β_{xxz}, β_{zzz}, β'_{xxz}, and β'_{zzz} for HF, and HCl calculated at the FCI/aug-cc-pVDZ level with the results obtained from the CCSD and CC3 calculations. All numbers in a.u.

	$\boldsymbol{\beta}$		$\boldsymbol{\beta}'$	
	xxz	*zzz*	*xxz*	*zzz*
HF:				
CCSD	−1.71	−12.15	−5.33	−53.79
CC3	−1.57	−11.67	−4.97	−51.97
FCI[a]	−1.55	−11.61	−4.89	−51.79
HCl:				
CCSD	−1.26	−28.32	10.88	−52.49
CC3	−0.91	−27.47	11.58	−50.47
FCI	−0.86	−27.28	11.63	−49.89

[a]In the case of HF, the FCI results for β are identical with those of Ref. 5.

absolute values of $\boldsymbol{\beta}$ or $\boldsymbol{\beta}'$ (such as the *xxz* componenents of HF and HCl), but even there the absolute deviations do not exceed 0.06 a.u. More significant differences occur between CCSD and FCI: the CCSD results are usually accurate within 5%–10% only.

For CO and LiF, the FCI calculations with aug-cc-pVDZ are not feasible. For these molecules we instead report the results from the finite difference CCSDT and CCSDTQ calculations for the β_{zzz} component. For CO, the coupled cluster series converges smoothly, as seen from Table VI, and the CC3 value is in error by less than 1% relative to the CCSDTQ result. In contrast to that and somewhat surprising, LiF turns out to be a difficult case. For the d-aug-cc-pVDZ basis the β_{zzz} CCSD result (see Table VI) is fortuitously close to the CCSDTQ result, while both CC3 and CCSDT significantly overestimate the β_{zzz} hyperpolarizability. In order to investigate this problem further, the accuracy of the CCSDTQ numbers was tested against FCI with a modified aug-cc-pVDZ basis set, where the most diffuse polarization functions were removed (denoted as aug'-cc-pVDZ in Table VI; see Sec. II). In this basis, the FCI calculations are feasible, but the β_{zzz} value is overestimated by 100% due to the use of a very small basis. However, the convergence properties of the coupled cluster series are similar to the one for the d-aug-pVDZ basis and it can be concluded that the relative error at the CCSDTQ level is below 1%. The reason for the slow convergence of the coupled cluster series for LiF is not obvious, since the LiF ground state wave function is much more single-reference dominated than, for example, the CO

TABLE VI. Comparison of β_{zzz} for CO, and LiF calculated from finite differences at the CCSDT and CCSDTQ level with the results obtained from the CCSD and CC3 calculations. See Sec. II for the definiton of aug′-cc-pVDZ basis. All numbers in a.u.

	CO	LiF	
	aug-cc-pVDZ	d-aug-cc-pVDZ	aug′-cc-pVDZ
CCSD	29.76	33.90	64.91
CC3	30.72	37.50	71.37
CCSDT	30.43	35.18	67.49
CCSDTQ	30.86	33.79	65.52
FCI	N/A	N/A	65.01

wave function. Also, the first singlet excited state (at about 6 eV) is well separated from the ground state. The hyperpolarizability of the LiF molecule certainly warrants further investigation. This, however, is beyond the scope of the present work.

The basis sets used in the above FCI and CCSDTQ benchmark calculations are somewhat too small for a full description of electron correlation. Thus, calculations in the coupled cluster hierarchies CCS, CC2, CCSD, and CC3 using the larger t-aug-cc-pVTZ have been performed to further investigate the convergence pattern in the *N*-electron space. The variation in the components of tensors $\boldsymbol{\beta}$ and $\boldsymbol{\beta}'$ for the coupled cluster wave function models is presented in Figs. 1–4 for HF, HCl, CO, and LiF, respectively.

The sensitivity of individual components to the correlation level is not uniform. For HF and HCl, β_{xxz} and β_{zxx} are more sensitive to correlation than β_{zzz}, in particular for the frequency dispersion effects. For HCl, SCF and CCS yield a wrong sign of frequency dipersion of β_{zxx} (Fig. 2). This is even more visible for the geometric derivatives β'_{xxz} and β'_{zxx}. Unlike for HF and HCl, β_{zzz} of CO and, in particular, its geometric derivative β'_{zzz} change more with the computational model than β_{xxz}, β_{zxx}, and their geometric derivatives do. For LiF, all components show extremely strong dependence on the correlation level (Fig. 4), in line with the previously discussed findings for smaller basis sets.

What immediately attracts attention is the nonmonotonic convergence of $\boldsymbol{\beta}$ and $\boldsymbol{\beta}'$ with respect to the electron correlation level: as a rule, CC2 overestimates the electron correlation effects, so that most of the graphs have extrema for CC2. In some cases, CC2 yields the results which are further away from the CC3 results than those from the SCF model. For example, for HF (Fig. 1) CC2 leads to a wrong sign of β'_{xxz} and β'_{zxx}, while SCF yields the sign consistent with CC3. For LiF (Fig. 4) CC2 gives the results which have the wrong order of magnitude for components of both $\boldsymbol{\beta}$ and $\boldsymbol{\beta}'$. The CCS and CC2 models tend to have large errors with opposite signs thus making the convergence towards CC3 (or FCI) nonmonotonic. Similar behavior has already been observed in previous studies on polarizabilities,[5,52] first hyperpolarizabilities,[5,23] and second hyperpolarizabilities.[30–32,53] It seems that in general the perturbation treatment in CC2 is not robust enough for calculation of high-order optical properties. It is perhaps not surprising, considering that CC2 response properties (unlike excitation energies) are correct only through first order in fluctuation potential.[14,54]

The effects of triples, measured as a difference between the CCSD and CC3 results, are larger for HCl (7% for β_{zzz}) than for HF (4% for β_{zzz}), compare also Figs. 1 and 2. The effects of triples are particularly large for β_{xxz} and β_{zxx} of CO (approximately 15%, see Fig. 3), and even larger for their geometric derivatives (150%, but here the absolute values are very small). For LiF, triples corrections are approximately 10% for the components of the $\boldsymbol{\beta}$ tensor, and twice as large for the components of the $\boldsymbol{\beta}'$ tensor. At this point, however, our observation from the first part of this section should be repeated that in the case of LiF CC3 (as well as CCSDT) overestimates the correlation effects beyond CCSD.

The calculated dispersion effects depend to some extent

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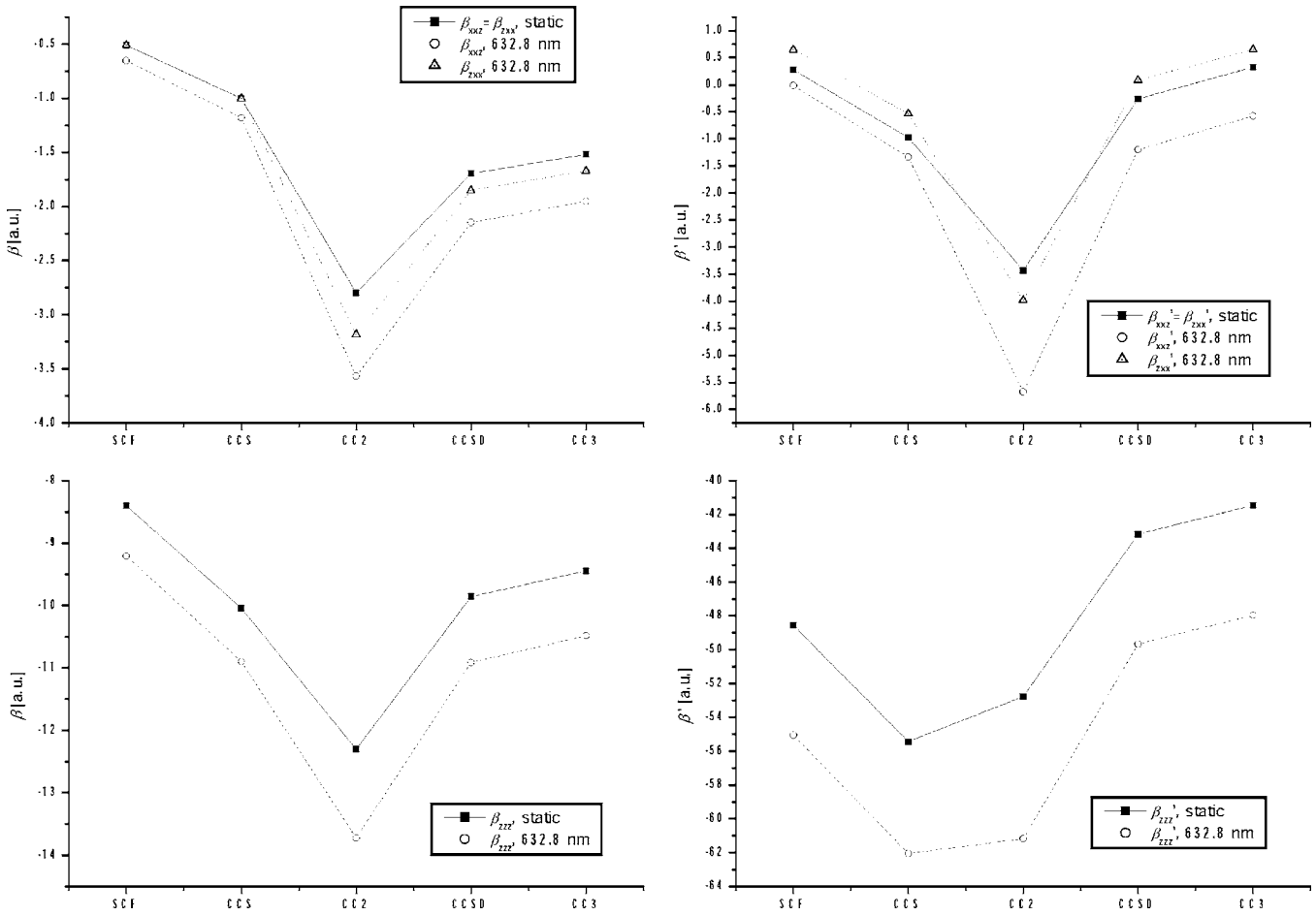


FIG. 1. HF: the components of the first hyperpolarizability β_{xxz}, β_{zxx}, and β_{zzz}, and their geometric derivatives β'_{xxz}, β'_{zxx}, and β'_{zzz} as a function of the wave function model. Basis set t-aug-cc-pVTZ (in a.u.).

on the level at which the electron correlation is accounted for. The largest relative differences between correlated methods occur for the cases where the high-order electron correlation effects are particularly large already for the static cases, that is, for LiF (the failure of CC2, see Fig. 4) and for the geometric derivatives of hyperpolarizability components for CO (large triples effects, see Fig. 3).

C. Core correlation effects

Another effect that is worth investigating is the core correlation contribution, usually neglected for optical properties. The core correlation effect has been estimated for HF, HCl, CO, and LiF by comparing the results from all-electron CCSD calculations (in the d-aug-cc-pCVTZ basis) and frozen core CCSD calculations (using the d-aug-cc-pVTZ basis), see Table VII. The employed basis sets had to be small enough to make all-electron calculations possible, so the observations here have qualitative rather than quantitative character.

For all systems under investigation, core correlation has a small influence on the components of the hyperpolarizability and its geometric derivative. As expected, the $\boldsymbol{\beta}'$ tensors are somewhat more sensitive to core correlation effects than the corresponding $\boldsymbol{\beta}$ tensors, but even for the components of $\boldsymbol{\beta}'$ the differences between the frozen core and all-electron calculations are small. The largest absolute core effects are observed for LiF where the hyperpolarizability is the largest. Predictably, the difference between the frozen core and all-electron CCSD calculations is larger for molecules with two heavy atoms (CO, LiF) than for those with one (HF, HCl). Core correlation affects in equal degree the static values and the frequency dispersion effects.

We conclude that taking into account the core correlation in calculations of the hyperpolarizability does not lead to improvements that in general justify the computational cost. Only when very high accuracy is required, it may be justified to consider the core correlation contribution, at least for the static values.

D. Extrapolation and comparison with DFT results

Having considered separately the effect of a more complete treatment of correlation and basis set effects it may be appropriate to use these investigations to make an estimate of values for $\boldsymbol{\beta}$ and $\boldsymbol{\beta}'$ that are fully converged with respect to both basis set limit and N-electron correlation limit. Starting out from the CC3/t-aug-cc-pVTZ results, and assuming that the effect of basis set extensions beyond t-aug-cc-pVTZ is similar for CC3 and CCSD, we may estimate the effect of extending the basis as β(CCSD/d-aug-cc-pV5Z)-β(CCSD/t-aug-cc-pVTZ). For LiF the d-aug-cc-pV5Z is re-

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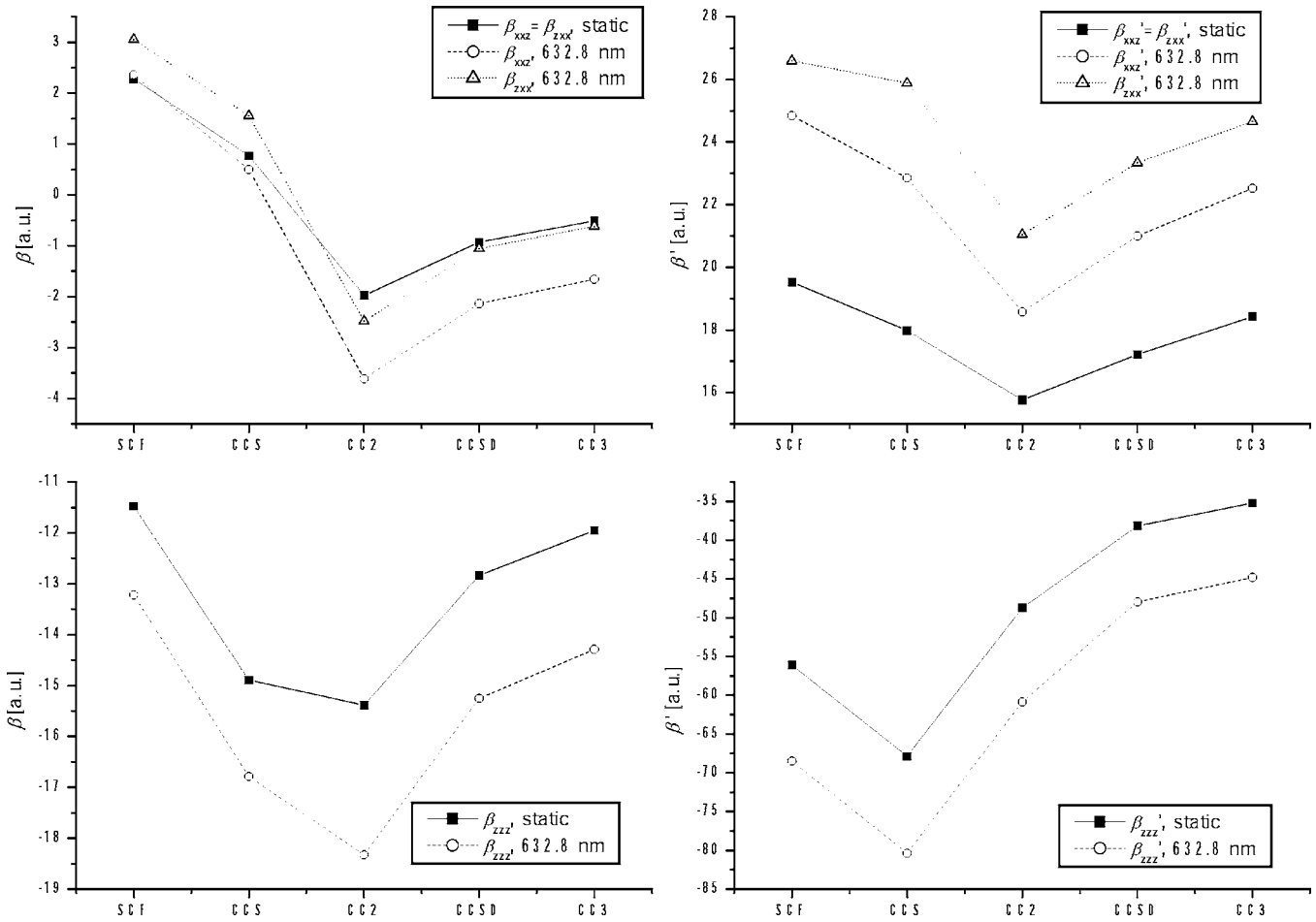


FIG. 2. HCl: the components of the first hyperpolarizability β_{xxz}, β_{zxx}, and β_{zzz}, and their geometric derivatives β'_{xxz}, β'_{zxx}, and β'_{zzz} as a function of the wave function model. Basis set t-aug-cc-pVTZ (in a.u.).

placed by t-aug-cc-pVQZ, and for HCl by d-aug-cc-pV6Z. The effects of core-valence correlation are estimated as a difference between the all-electron and frozen core CCSD results obtained with d-aug-cc-pCVTZ and d-aug-cc-pVTZ basis sets, respectively. The uncertainties of the estimates are rather broad, since they are set equal to the added contributions plus the correlation contribution beyond CC3:

$$\begin{aligned}\beta_{\text{extrap}} &= \beta(\text{CC3/t-aug-cc-pVTZ}) \\ &+ [\beta(\text{CCSD/d-aug-cc-pV5Z}) \\ &- \beta(\text{CCSD/t-aug-cc-pVTZ})] \\ &+ [\beta(\text{CCSD(AE)/d-aug-cc-pCVTZ}) \\ &- \beta(\text{CCSD(FC)/d-aug-cc-pVTZ})]. \end{aligned} \quad (1)$$

The extrapolated average parallel hyperpolarizabilities $\beta_{\parallel}$,

$$\beta_{\parallel} = \tfrac{1}{5}(3\beta_{zzz} + 2\beta_{zxx} + 4\beta_{xxz}), \quad (2)$$

and their geometric derivatives are shown in Table VIII, together with the CCSD and CC3 numbers. We have also tabulated the vibrational corrections available from the literature.[10,13,55]

In Table VIII we also report the experimental hyperpolarizabilities for HF, HCl, and CO. Comparing the experimental and calculated hyperpolarizabilities of HF (electronic part plus the vibrational correction[55] results in −9.50 a.u.) we note that the consideration of triples has not made the hyperpolarizability closer to the experimental value. The extrapolated HF result is outside the experimental error bar, although it is within the range of three times the experimental error bar. It would therefore have been instructive to have more precise experimental result, and we agree with conclusions of Gauss *et al.*,[1] who have previously carried out very accurate calculations of the electronic frequency-dependent hyperpolarizability of HF using the CC3 model (and adding the literature vibrational contributions) and expressed the need for an experimental reinvestigation on HF. For HCl, the best estimate for the electronic contribution plus vibrational contributions from the literature[13] result in −9.11 a.u., within the error bar of the experiment (the vibrational contributions for HF and HCl in Ref. 24 have been quoted erroneously). For CO the extrapolated hyperpolarizabilities are inside the experimental error bars (although we note that the vibrational contributions are not complete), and for LiF no experimental hyperpolarizabilities are available. While the pure electronic contribution to the hyperpolarizabilities have been determined accurately, comparison with experimental polarizabilities require considerations of the vibrational contributions. In particular, the pure vibrational contribution may give difficulties as for optical frequencies close to vibrational transitions perturbation theory may break down. The experi-

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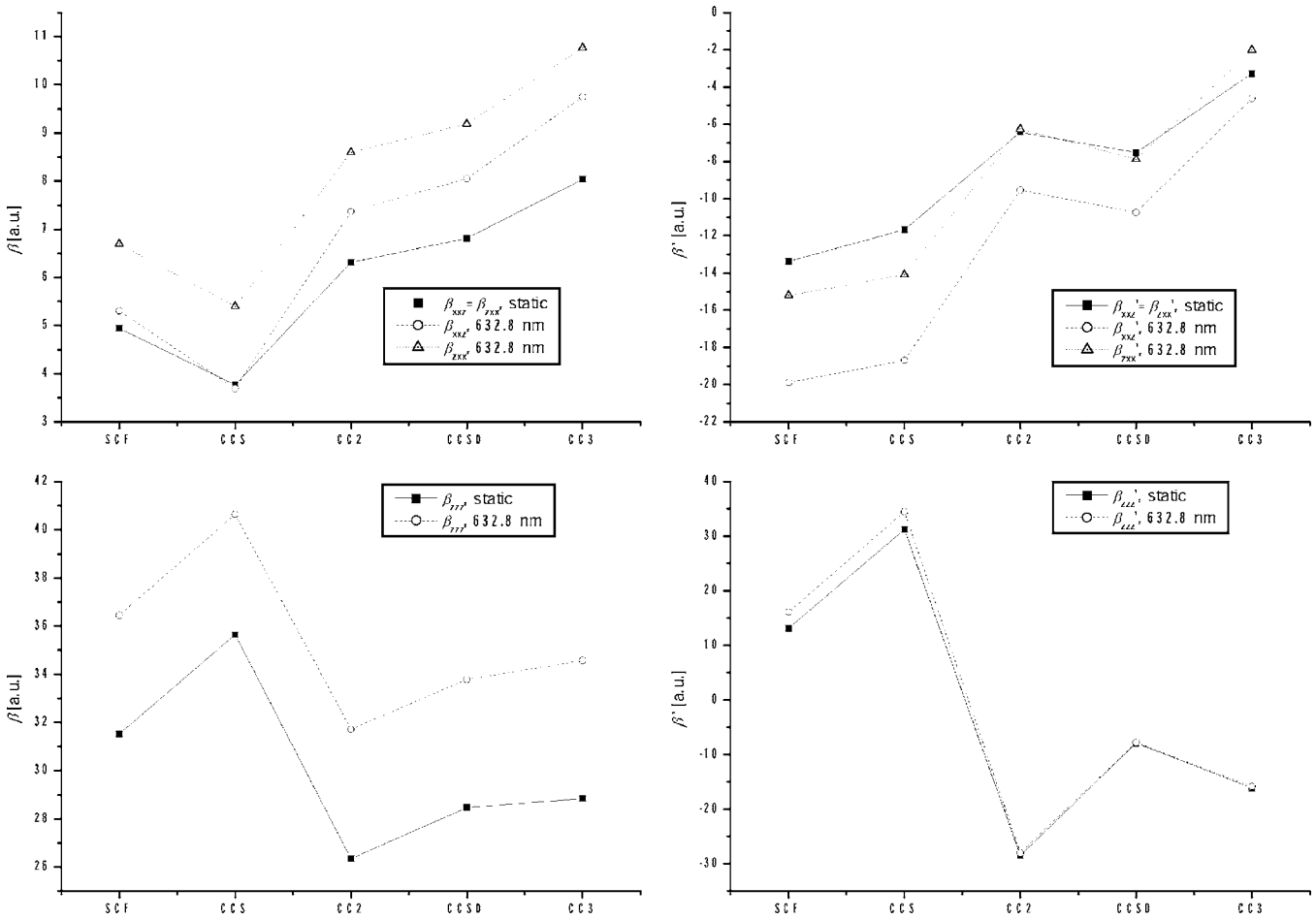


FIG. 3. CO: the components of the first hyperpolarizability β_{xxz}, β_{zxx}, and β_{zzz}, and their geometric derivatives β'_{xxz}, β'_{zxx}, and β'_{zzz} as a function of the wave function model. Basis set t-aug-cc-pVTZ (in a.u.).

mental determination may also be hampered by uncertainties related to temperature and pressure extrapolations and to the fact that measurements are relative, in the case of HF and HCl,[56] to the CF_4 hyperpolarizability which is not accurately known. Considering that the experimental hyperpolarizabilities are rather dated and given the difficulties in the experimental and theoretical determinations it remains unclear whether the theoretical extrapolated hyperpolarizabilities with calculated vibrational contributions or the experimental hyperpolarizabilities are the most accurate. Certainly for benchmarking DFT hyperpolarizabilities the extrapolated hyperpolarizabilities should be used since a direct comparison can then be made between the electronic contributions obtained using the two approaches.

The conclusions drawn in Ref. 24 with respect to the accuracy of the LDA, BLYP, and B3LYP hyperpolarizabilities are still valid, and B3LYP is the functional which renders the results closest to the ones obtained using the coupled cluster model. This is also in agreement with Ref. 23, where, however, again only LDA, BLYP, and B3LYP functionals have been tested. Out of the functionals tested in the present work, PBE0 performs very satisfactorily for the hyperpolarizabilities, although the case of CO is an exception. Another functional which is reliable in this respect (although it seems inferior to B3LYP) is BPW91. LiF is apparently a difficult molecule for density functional theory, and many functionals fail in this case completely. The exceptions are PBE0, B3LYP, and B3P86, but good agreement of the last one with CC may be coincidental, given its poor performance for other molecules.

The situation is less clear for the geometric derivatives of the hyperpolarizabilities. For HCl all functionals under study fail to render the geometric derivative of the hyperpolarizability in agreement with the coupled cluster (or extrapolated) results. For HF and CO, the best agreement with the advanced correlated methods is obtained, almost certainly coincidentally, for a pure Hartree-Fock wave function, although for $\beta'_{\|}$ of CO PBE0 also seems to perform well (rather surprisingly, since it does not for $\beta_{\|}$ of CO). For LiF most of the functionals, except for B3P86 and PBE0, give results that are nearly one order of magnitude too large. All together it appears that none of the considered DFT potentials can be used to obtain geometric derivatives of the hyperpolarizabilities in a reliable fashion, although PBE0 seems to perform better than most.

IV. SUMMARY AND CONCLUSIONS

The calculations of second harmonic generation hyperpolarizabilities and their geometric derivatives have been carried out in the hierarchy of coupled cluster wave functions, ranging from CCS to CC3, the latter including triple

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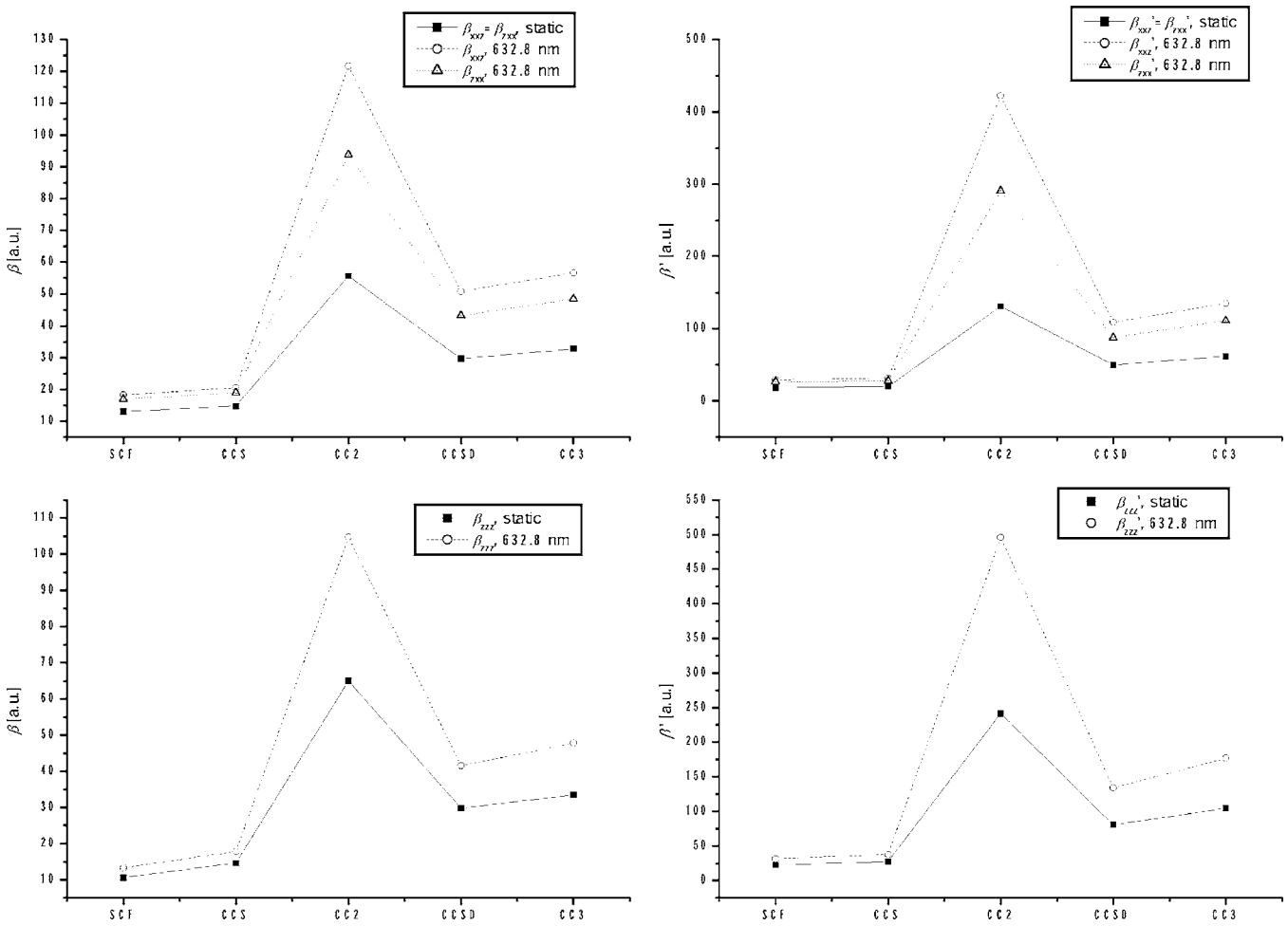


FIG. 4. LiF: the components of the first hyperpolarizability β_{xxz}, β_{zxx}, and β_{zzz}, and their geometric derivatives β'_{xxz}, β'_{zxx}, and β'_{zzz} as a function of the wave function model. Basis set t-aug-cc-pVTZ (in a.u.).

excitations in an iterative approximate way.[28,29] Additionally, FCI calculations for HF, HCl and LiF have been carried out, as well as finite field calculations at the CCSDT and CCSDTQ level for CO and LiF. Core correlation effects have been investigated at the CCSD level. The results of these high-level *ab initio* calculations have been compared with density functional theory. The main observations can be summarized as follows.

The studies of the basis set convergence allow us to expect that the errors resulting from the basis set incompleteness do not exceed 5% for our best values, in most cases they should be smaller. The high-order electron correlation effects tend to be more significant. The calculations in the coupled cluster hierarchy indicate that the triples effects as rendered by CC3 are as a rule approximately 5%–10% for the components of hyperpolarizability tensor, but they tend to be larger for geometric derivatives. Comparison with FCI and finite field CCSDTQ calculations indicate that CC3 is close to convergence in N-electron space for HF, HCl, and CO. LiF, however, turns out to be a difficult case: rather unexpectedly, as near-degeneracy effects can be excluded for this molecule, the CCSDT result fails by around 4% and the approximate treatment of triples in CC3 further increases this error in β to about 10%. The reason for this failure of CC3 (and CCSDT) remains unclear and should be further investigated.

Core-valence correlation, as estimated at the CCSD level, has small influence on the tensor of first hyperpolarizability, but its geometric derivatives are somewhat more sensitive to this effect. Therefore, it may be advisable to take core-valence correlation into account in the calculations of the vibrational part of the hyperpolarizability if high accuracy is desired.

The obtained results have been used to extrapolate the values of hyperpolarizabilities and their geometric derivatives. The present study was partly motivated by the need to compare the numbers obtained by means of density functional theory in Ref. 24 with benchmark results of higher quality than CCSD. Some other functionals, not investigated in Ref. 24, were included in the comparison.

There are three exchange-correlation functionals which seem to perform well for first hyperpolarizabilities, and which give significant improvement with respect to HF-SCF: B3LYP, BPW91, and PBE0. B3LYP seems to render good results most consistently: PBE0 fails for CO, and BPW91 for LiF. The situation is somewhat less clear for the geometric derivatives of the hyperpolarizabilities, since the performance of DFT is very inconsistent, and for HCl all DFT functionals fail.

One should realize that the above conclusions have been based on the results obtained for small molecules. The com-

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TABLE VII. Comparison of CCSD results for first hyperpolarizability (β) and its geometric derivative (β'), obtained using frozen core (FC) and all-electron (AE) models, with d-aug-cc-pVTZ and d-aug-cc-pCVTZ basis sets, respectively. Static results (infinite wavelength) and a difference between the static results and the results for the optical wavelength of 514.5 nm (disp) are shown. All values in a.u.

	β tensor				β' tensor			
	0 freq		disp		0 freq		disp	
	FC	AE	FC	AE	FC	AE	FC	AE
				Hydrogen fluoride				
xxz	−1.52	−1.51	−0.77	−0.75	−0.06	−0.13	−1.81	−1.79
zxx	−1.52	−1.51	−0.23	−0.22	−0.06	−0.13	0.62	0.61
zzz	−9.77	−9.74	−1.67	−1.66	−43.27	−43.31	−10.39	−10.35
				Hydrogen chloride				
xxz	−1.16	−1.05	−2.47	−2.32	17.43	17.21	4.84	4.90
zxx	−1.16	−1.05	−0.27	−0.21	17.43	17.21	10.48	10.39
zzz	−12.74	−12.62	−3.91	−3.84	−38.78	−39.38	−16.25	−16.28
				Carbon oxide				
xxz	7.01	6.96	2.07	2.00	−6.96	−7.07	−5.44	−5.64
zxx	7.01	6.96	4.00	3.95	−6.96	−7.07	−0.22	−0.32
zzz	28.36	28.21	8.64	8.54	−8.36	−8.31	−0.05	−0.03
				Lithium fluoride				
xxz	29.65	28.75	44.90	44.01	50.43	49.05	148.55	145.15
zxx	29.65	28.75	24.51	23.95	50.43	49.05	75.31	73.32
zzz	29.67	28.73	21.57	20.86	80.05	79.16	106.37	103.27

putational requirements for optical properties of large molecules tend to be less stringent than for the small ones, on account on the former being dominated by intramolecular charge transfer effects rather than by excitations into diffuse Rydberg-like states, as in the case of the latter. For large molecules, the (hyper)polarizabilities thus converge much faster with the basis set and are usually less sensitive to correlation effects. Therefore, it is likely that performance of computational methods under study would be somewhat better for larger molecules.

While the high accuracy of the methods like CC3 would carry over to systems of an arbitrary size, these methods are prohibitively expensive for medium-size and large molecules, thus the need for lower-scaling methods. DFT is currently the best choice for the calculation of the high-order optical properties of medium-size and large molecules, and the efforts should be directed towards the development of more accurate functionals. On the other hand, lowering the scaling of highly accurate CC models so that they can address at least medium-size molecules would be highly desired.

TABLE VIII. Comparison of average parallel hyperpolarizability $\beta_\parallel$ and its geometric derivative $\beta'_\parallel$ calculated for the wavelength 694.3 nm in the t-aug-cc-pVTZ basis. See Sec. III D for the details of extrapolation. All values in a.u.

	LDA	BLYP	B3LYP	B3P86	BP86	BPW91	OLYP	PBE0	PBE	HF	CCSD	CC3	Extrap.	Expt.	Vib.
								$\beta_\parallel$							
HF	−10.58	−10.44	−8.67	−6.30	−6.70	−8.84	−9.51	−7.29	−9.21	−6.14	−8.81	−8.33	−8.14±0.96	−10.9±0.95[a]	−1.36[b]
HCl	−15.42	−13.29	−10.53	−6.84	−10.17	−12.11	−13.25	−9.79	−13.23	−4.69	−10.77	−9.65	−8.87±0.25	−9.9±1.25[a]	−0.24[c]
CO	36.83	36.44	33.07	25.59	26.41	29.47	33.61	26.51	29.34	28.06	29.40	31.71	31.29±3.59	30.2±3.2[d]	−0.08[e]
LiF	199.28	301.04	129.45	90.02	178.55	207.35	599.70	95.69	241.30	27.88	76.16	85.52	81.43±12.23	⋯	⋯
								$\beta'_\parallel$							
HF	−21.64	−25.15	−38.98	−24.06	−7.21	−12.75	⋯[f]	−15.80	−10.76	−32.05	−29.87	−28.11	−28.31±2.89	⋯	⋯
HCl	9.76	20.96	15.24	14.02	⋯	15.05	16.24	9.07	18.12	−10.54	−2.48	1.08	−1.39±0.82	⋯	⋯
CO	−20.88	−38.20	−22.15	−21.62	−26.17	−19.42	−23.64	−16.00	−19.05	−11.42	−15.93	−13.98	−13.44±1.90	⋯	⋯
LiF	724.11	1463.71	783.04	291.81	798.39	844.62	⋯[f]	259.31	1034.89	49.26	179.06	227.90	219.9±30.01	⋯	⋯

[a]Reference 56.
[b]Reference 55, a sum of zero-point vibrational correction (−0.72 a.u.) and pure vibrational contribution (−0.64), calculated with CCSD/t-aug-cc-pVTZ frequency-dependent properties and a CCSD(T)/t-aug-cc-pVTZ potential.
[c]Reference 13, a sum of zero-point vibrational correction (0.16) and pure vibrational contribution (−0.4), calculated with CC3/d-aug-cc-pVTZ frequency-dependent properties and a CCSD(T)/aug-cc-pVQZ potential.
[d]Reference 15.
[e]Reference 10, zero-point correction calculated in the static limit by means of CCSD(T) with the 6*s*4*p*4*d*2*f* basis set.
[f]In these cases, we could not converge response calculations tight enough to perform numerical differentiation with respect to bond length.

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