

A comparison of density-functional-theory and coupled-cluster frequency-dependent polarizabilities and hyperpolarizabilities^{||}

PAWEŁ SALEK^{†,¶}, TRYGVE HELGAKER^{†,*}, OLAV VAHTRAS[‡], HANS ÅGREN[‡],
DAN JONSSON^{§,⊥} and JÜRGEN GAUSS[§]

[†]Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo, Norway

[‡]Laboratory of Theoretical Chemistry, The Royal Institute of Technology, SE-10044 Stockholm, Sweden

[§]Institut für Physikalische Chemie, Universität Mainz, D-55099 Mainz, Germany

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The frequency-dependent polarizabilities and hyperpolarizabilities of HF, CO, H₂O and para-nitroaniline calculated by density-functional theory are compared with accurate coupled-cluster results. Whereas the local-density approximation and the generalized gradient approximation (BLYP) perform very similarly and overestimate polarizabilities and, in particular, the hyperpolarizabilities, hybrid density-functional theory (B3LYP) performs better and produces results similar to those obtained by coupled-cluster singles-and-doubles theory. Comparisons are also made for singlet excitation energies, calculated using linear response theory.

1. Introduction

With recent developments in density-functional theory (DFT), it has become possible to calculate frequency-dependent polarizabilities and hyperpolarizabilities routinely within the adiabatic approximation. In particular, such calculations may now be carried out using the local-density approximation (LDA), the generalized gradient approximation (GGA), and hybrid DFT (in which some proportion of Hartree–Fock exchange is included in the energy). An advantage of these DFT methods over the traditional wave-function methods is that they may be applied to large systems, currently intractable by high-level coupled-cluster theory, thus greatly expanding the application range of quantum-chemical methods for the calculation of frequency-dependent molecular properties. However, for DFT to become a useful tool for the study of frequency-dependent polarizabilities and hyperpolarizabilities, it is necessary first to establish its level of accuracy for these properties. Although much information about the performance of DFT for such properties may be gained by comparison with experimental results, for

some purposes it is better to make a comparison with results from high-level *ab initio* methods such as coupled-cluster theory. In this manner, problems related to the description of vibrational contributions and solvent effects (both of which may be large) are avoided, allowing us to explore directly the accuracy of the electronic description. Such an approach is taken in the present paper. Although we cover both polarizabilities and hyperpolarizabilities, our emphasis is on the latter property, which has been much less studied by DFT than polarizabilities. In addition, in view of their close relationship to polarizabilities and hyperpolarizabilities, we have taken the opportunity to compare DFT singlet excitation energies with those calculated from coupled-cluster theory, for the same molecules and the same basis sets as used for the polarizabilities.

Hyperpolarizabilities were first studied by DFT at the LDA level in the static limit by Chong in 1992 and by Guan *et al.* in 1993, using a finite-difference technique [1, 2]. In 1996, Dickson and Becke carried out a more extensive study of hyperpolarizabilities, establishing the numerical LDA limit and concluding that large basis sets are needed for the accurate calculation of such properties [3]. The first calculations of frequency-dependent hyperpolarizabilities are those carried out by Gisbergen *et al.* in 1998 using adiabatic LDA (ALDA) [4]. In this approximation, LDA is used for the response of the electron density, irrespective of how the density itself is calculated. The calculations presented by Gisbergen *et al.* showed

^{||} Dedicated to Prof. N.C. Handy.

[¶] Present address: Laboratory of Theoretical Chemistry, The Royal Institute of Technology, SE-10044 Stockholm, Sweden.

[⊥] Department of Physics, Stockholm University, AlbaNova, SE-10691, Stockholm, Sweden.

*Correspondence author. e-mail: trygve.helgaker@kjemi.uio.no

that ALDA strongly overestimates frequency-dependent hyperpolarizabilities.

In 1999, Cohen *et al.* presented a careful comparison of LDA, GGA, and hybrid hyperpolarizabilities in the static limit [5]. In addition to confirming the validity of ALDA (by the very similar results obtained for LDA and GGA), these authors found that the inclusion of exact exchange in the calculations improved the quality of the calculated hyperpolarizabilities. Moreover, Cohen *et al.* carried out calculations with the asymptotic correction (AC) [6] grafted on to the exchange-correlation potential. Although the results of these AC calculations were slightly erratic, the improvement was sufficiently substantial to demonstrate the need for a correct description of the asymptotic region in calculations of polarizabilities and hyperpolarizabilities. Frequency-dependent hyperpolarizabilities beyond ALDA were presented by Salek *et al.* in 2002 using a recently developed code for the calculation of quadratic response functions at the LDA, GGA, and hybrid levels of DFT [7].

In the present paper, we compare singlet excitation energies, the frequency-dependent polarizabilities, and the first frequency-dependent hyperpolarizabilities of HF, CO, and H₂O calculated at the Hartree–Fock, LDA [8, 9], Becke–Lee–Yang–Parr (BLYP) [10, 11], and the hybrid three-parameter (B3LYP) [12, 13] levels of theory with the results obtained with coupled-cluster singles (CCS), CC2 [14], coupled-cluster singles-and-doubles (CCSD) [15], and CC3 [16] theories. Although the coupled-cluster excitation energies of all molecules and the coupled-cluster polarizabilities of HF were calculated specifically for this paper, the remaining coupled-cluster results with which our comparisons are made are those presented by Gauss *et al.* [17] for the HF molecule and by Christiansen *et al.* [18] for the CO and H₂O molecules. In all calculations on these molecules, we have used the same basis sets and geometries as in the papers by these authors. All DFT calculations have been carried out within the adiabatic approximation—that is, the time-dependent functional is assumed to depend on the time-dependent density in the same manner as the time-independent functional depends on the time-independent density.

We also present in this paper calculations of the static and frequency-dependent first hyperpolarizability of the *para*-nitroaniline molecule (PNA). With an NH₂ donor and an NO₂ acceptor substituted on a phenyl ring, this molecule shows an exceptionally strong charge-transfer character accompanied by a large polarizability and hyperpolarizability. It has served in the past as an important test system for experimental and theoretical investigations of hyperpolarizabilities and therefore is an interesting system for a comparison of the performance

of DFT and coupled-cluster methods for such properties [7].

The bulk of this paper contains three parts. The main results for the small molecules HF, CO, and H₂O and the large molecule PNA are presented and discussed in section 3, following a short discussion of technical details in section 2. Our main conclusions are given in section 4.

2. Computational details

All Hartree–Fock and DFT calculations presented in this paper have been carried out with a modified version of the Dalton program [19], as described in [7], using the same geometries and basis sets as in [17, 18]. The coupled-cluster results not taken from [17, 18] were obtained with the Mainz–Austin–Budapest version of ACES II [20] using the implementations described in [17, 21], except for the CCS results, which were obtained with the Dalton program.

For the HF molecule, we used the triply augmented polarized valence triple-zeta (t-aug-cc-pVTZ) basis of Woon and Dunning [22], whereas the slightly smaller doubly augmented polarized valence triple-zeta (d-aug-cc-pVTZ) basis of Woon and Dunning was used for the CO and H₂O molecules. All calculations were carried out at the experimental equilibrium geometries. The HF and CO molecules were oriented along the *z* axis, with bond distances of 1.7328 and 2.132 a_0 , whereas the H₂O molecule was oriented in the *xz* plane along the *z* axis, with a OH bond distance of 0.957 Å and a HOH bond angle of 104.5°. In all cases, the most electronegative atom (F or O) is on the negative *z* axis.

In our B3LYP calculations on PNA, we used the cc-pVDZ basis, the aug-cc-pVDZ basis and the Sadlej basis [23] (optimized for polarizability calculations) contracted as [10s6p4d|5s3p2d] and [6s4p|3s2p]. In the CCSD calculations on PNA, we used the standard correlation-consistent basis sets cc-pVDZ and cc-pVTZ, augmented with diffuse functions. In some cases, we used a stripped down augmented basis set, with the most diffuse *d* functions on the hydrogen atoms and the most diffuse *f* functions on the other atoms removed. As in previous PNA calculations, we adopt a planar C_{2v} geometry [24, 25]. The coordinates were obtained from crystallographic data [26], supplemented with two additional coordinates to determine the geometry uniquely [27]—see table 1 of [25]. For all frequencies considered here, the assumption of Kleinmann symmetry holds well, the deviation being negligible even for the largest frequency of 1.494 eV.

3 Results

We begin this section by comparing the singlet DFT and coupled-cluster excitation energies of HF, CO, and H₂O in section 3.1. Next, we consider in a similar manner the frequency-dependent polarizabilities and hyperpolarizabilities of these molecules in sections 3.2 and 3.3, respectively. After a brief discussion of the dispersion of the calculated polarizabilities and hyperpolarizabilities in section 3.4, we conclude by discussing the frequency-dependent first hyperpolarizability of the PNA molecule in section 3.5.

3.1 Singlet excitation energies of HF, CO, and H₂O

In tables 1–3, we have listed the lowest two calculated excitation energies of the different irreducible representations of the point groups of HF, CO, and H₂O,

respectively. In table 4, we have listed some statistical measures of errors in the calculated excitation energies, relative to the excitation energies calculated at the CC3 level of theory.

Concerning first the coupled-cluster results, we note that the CCS model with a mean absolute error of 9.6% in the calculated excitation energies performs no better than the Hartree–Fock model with an error of 9.5%, whereas the CC2 and CCSD results deviate by 4.7% and 0.7%, respectively, from the CC3 results. As a general trend, the excitation energies decrease as the quality of the description is improved by including higher connected excitations, although many exceptions are observed. Since the CCSD model gives excitation energies that differ by only 0.1–0.3 eV from the CC3 results, we conclude that the CC3 excitation energies are within about 0.1 eV of the full configuration-interaction (FCI) results. The basis-set errors are more difficult to

Table 1. Singlet excitation energies (eV) of HF in the t-aug-cc-pVTZ basis.

Sym.	HF	CCS	CC2	CCSD	CC3	LDA	BLYP	B3LYP
Σ^+	14.85	14.88	12.49	13.39	13.45	10.06	9.76	11.20
	15.66	15.72	13.51	14.50	14.58	10.40	10.08	11.53
Σ^-	14.76	14.78	12.43	13.24	13.32	10.07	9.80	11.20
	16.20	16.20	13.53	14.53	14.61	10.39	10.10	11.55
Π	11.69	11.74	9.94	10.42	10.45	8.98	8.63	9.44
	14.55	14.57	12.35	13.10	13.17	9.87	9.60	11.13
Δ	14.74	14.76	12.40	13.20	13.27	10.06	9.76	11.17
	16.18	16.18	13.51	14.51	14.59	10.38	10.06	11.50

Table 2. Singlet excitation energies (eV) of CO in the d-aug-cc-pVTZ basis.

Sym.	HF	CCS	CC2	CCSD	CC3	LDA	BLYP	B3LYP
Σ^+	11.87	11.90	10.82	10.96	10.67	9.22	8.94	9.80
	12.55	12.56	11.40	11.57	11.28	9.50	9.25	10.15
Σ^-	9.37	9.72	10.39	10.09	10.09	9.88	9.77	9.72
	14.88	14.88	14.37	14.51	14.49	12.55	12.03	12.92
Π	8.78	9.06	8.67	8.62	8.52	8.17	8.22	8.39
	12.59	12.59	11.52	11.70	11.41	9.54	9.31	10.21
Δ	9.92	10.12	10.70	10.23	10.22	10.33	10.00	10.03
	13.82	13.82	12.76	12.93	12.63	11.10	10.80	11.61

Table 3. Singlet excitation energies (eV) of H₂O in the d-aug-cc-pVTZ basis.

Sym.	HF	CCS	CC2	CCSD	CC3	LDA	BLYP	B3LYP
A_1	10.88	10.90	9.40	9.88	9.90	8.06	7.71	8.67
	11.43	11.47	9.66	10.23	10.24	8.63	8.37	9.08
A_2	10.32	10.36	8.89	9.37	9.38	7.61	7.33	8.24
	12.11	12.12	10.25	10.91	10.94	8.10	7.86	8.90
B_1	12.47	12.48	10.51	11.20	11.24	9.07	8.68	9.67
	12.63	12.66	11.19	11.70	11.72	9.63	9.41	10.35
B_2	8.65	8.69	7.25	7.61	7.62	6.56	6.25	6.90
	11.15	11.16	9.43	10.01	10.04	7.76	7.54	8.59

Table 4. Statistics relative to CC3 (%) for the singlet excitation energies of HF, CO, and H₂O.

	HF	CCS	CC2	CCSD	LDA	BLYP	B3LYP
$\overline{\Delta}$	8.6	9.2	-3.5	0.2	-17.9	-20.3	-12.3
$\overline{\Delta}_{\text{std}}$	4.9	4.2	3.9	1.1	8.2	8.3	5.5
$ \overline{\Delta} $	9.5	9.6	4.7	0.7	17.9	20.3	12.3
$ \Delta _{\text{max}}$	13.5	14.0	7.4	2.7	28.9	31.0	21.2

Table 5. The frequency-dependent polarizability (atomic units) of HF in the t-aug-cc-pVTZ basis, with the z axis as the molecular axis.

HF		HF	CCS	CC2	CCSD	CC3	LDA	BLYP	B3LYP
α_{zz}	∞	5.76	6.06	6.79	6.41	6.39	6.85	6.97	6.59
	694.3 nm	5.80	6.10	6.85	6.47	6.44	6.92	7.05	6.66
	632.8 nm	5.81	6.11	6.86	6.48	6.45	6.94	7.06	6.67
α_{xx}	∞	4.49	4.67	5.66	5.25	5.25	5.93	6.02	5.53
	694.3 nm	4.53	4.71	5.73	5.31	5.31	6.01	6.11	5.60
	632.8 nm	4.54	4.72	5.74	5.32	5.32	6.03	6.13	5.61
α	∞	4.92	5.13	6.04	5.64	5.63	6.24	6.34	5.89
	694.3 nm	4.95	5.17	6.10	5.69	5.69	6.32	6.42	5.95
	632.8 nm	4.96	5.18	6.12	5.70	5.70	6.33	6.44	5.97
$\Delta\alpha$	∞	1.26	1.39	1.13	1.16	1.13	0.92	0.95	1.06
	694.3 nm	1.27	1.40	1.12	1.16	1.13	0.91	0.94	1.06
	632.8 nm	1.27	1.40	1.12	1.16	1.13	0.91	0.93	1.06

estimate but are probably no larger than 0.2 eV. Moreover, although the basis-set requirements are stricter in coupled-cluster theory than in DFT, the basis-set errors will largely cancel as we compare the results obtained by different methods. We conclude that a comparison of the DFT results with the CC3 results gives a good indication of the overall performance of DFT for the calculation of excitation energies.

Turning our attention to DFT, we note that the quality of the excitation energies obtained at the LDA, BLYP, and B3LYP levels of theory is modest, with mean absolute errors relative to CC3 of 18%, 20%, and 12%, respectively. Except for one LDA excitation energy in the CO molecule, all excitation energies are underestimated by DFT. This well-established behaviour of DFT is in contrast to that of Hartree–Fock theory, for which most excitation energies are overestimated. We note that DFT performs slightly better for CO than for the other molecules. Thus, whereas the B3LYP functional gives mean absolute and maximum errors of 0.8 and 1.6 eV for CO, respectively, the corresponding errors for HF are 2.3 and 3.1 eV. In general, the hybrid B3LYP functional performs much better than the LDA and BLYP functionals, its errors relative to the CC3 model being only two-thirds of the LDA and BLYP errors.

3.2 The frequency-dependent polarizabilities of HF, CO, and H₂O

In tables 5–7, we have listed the polarizabilities of HF, CO, and H₂O, calculated in the static limit and at wavelengths of 694.3 and 632.8 nm. In addition to the Cartesian components α_{ij} , we have listed the isotropic and anisotropic components defined as

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}), \quad (1)$$

$$\Delta\alpha = \sqrt{\frac{(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2}{2}}. \quad (2)$$

As for the excitation energies in section 3.1, we have, in table 8, listed statistical measures of errors in the Cartesian components of the polarizability tensors (relative to CC3). We note that the CCSD components deviate from the CC3 components by about 0.4%, which is less than the deviation of 1.2% observed for the excitation energies. The basis-set errors in the CC3 polarizabilities have been estimated to be less than 1% [18]. We conclude that the CC3 polarizabilities are within about 1% of the true polarizabilities for these systems.

Whereas the Hartree–Fock model underestimates the polarizabilities by about 10%, the LDA and BLYP

Table 6. The frequency-dependent polarizability (atomic units) of CO in the d-aug-cc-pVTZ basis, with the z axis as the molecular axis. The coupled-cluster values have been taken from [18].

CO		HF	CCS	CC2	CCSD	CC3	LDA	BLYP	B3LYP
α_{zz}	∞	14.49	15.26	16.10	15.71	15.51	15.91	16.05	15.54
	694.3 nm	14.67	15.43	16.33	15.92	15.73	16.16	16.31	15.77
	632.8 nm	14.71	15.47	16.38	15.97	15.77	16.21	16.36	15.82
α_{xx}	∞	11.27	12.09	12.15	11.87	11.94	12.61	12.60	12.16
	694.3 nm	11.46	12.28	12.37	12.07	12.16	12.87	12.85	12.39
	632.8 nm	11.50	12.32	12.41	12.12	12.21	12.93	12.91	12.44
α	∞	12.34	13.15	13.47	13.15	13.13	13.71	13.75	13.29
	694.3 nm	12.53	13.33	13.69	13.35	13.35	13.97	14.00	13.52
	632.8 nm	12.57	13.37	13.73	13.40	13.40	14.02	14.06	13.57
$\Delta\alpha$	∞	3.22	3.17	3.95	3.84	3.57	3.30	3.45	3.38
	694.3 nm	3.21	3.15	3.96	3.85	3.57	3.29	3.46	3.38
	632.8 nm	3.21	3.15	3.97	3.85	3.56	3.28	3.45	3.38

Table 7. The frequency-dependent polarizability (atomic units) of H₂O in the d-aug-cc-pVTZ basis, with the molecule in the xz plane and the z axis as the symmetry axis. The coupled-cluster values have been taken from [18].

H ₂ O		HF	CCS	CC2	CCSD	CC3	LDA	BLYP	B3LYP
α_{xx}	∞	7.91	8.26	10.15	9.35	9.38	10.63	10.77	9.81
	694.3 nm	8.03	8.37	10.40	9.55	9.58	10.94	11.11	10.06
	632.8 nm	8.05	8.40	10.45	9.59	9.63	11.01	11.19	10.11
α_{yy}	∞	9.18	9.71	10.52	9.98	9.95	10.58	10.72	10.22
	694.3 nm	9.27	9.81	10.65	10.09	10.07	10.72	10.87	10.35
	632.8 nm	9.29	9.83	10.68	10.11	10.09	10.75	10.90	10.37
α_{zz}	∞	8.51	8.97	10.28	9.61	9.61	10.57	10.67	9.98
	694.3 nm	8.62	9.07	10.45	9.75	9.76	10.77	10.88	10.15
	632.8 nm	8.64	9.10	10.48	9.78	9.79	10.82	10.93	10.18
α	∞	8.53	8.98	10.32	9.65	9.65	10.59	10.72	10.00
	694.3 nm	8.64	9.08	10.50	9.80	9.80	10.81	10.95	10.19
	632.8 nm	8.66	9.11	10.54	9.83	9.84	10.86	11.01	10.22
$\Delta\alpha$	∞	1.10	1.26	0.33	0.55	0.50	0.06	0.09	0.36
	694.3 nm	1.07	1.25	0.23	0.47	0.43	0.20	0.24	0.26
	632.8 nm	1.07	1.24	0.22	0.46	0.40	0.23	0.28	0.23

Table 8. Statistics relative to CC3 (%) for all Cartesian components of the polarizabilities of HF, CO, and H₂O in the static limit and at the wavelengths 694.3 and 632.8 nm.

	HF	CCS	CC2	CCSD	LDA	BLYP	B3LYP
$\bar{\Delta}$	-10.4	-5.6	5.9	0.1	8.5	9.8	3.2
Δ_{std}	3.8	4.7	2.2	0.6	3.9	4.3	1.7
$ \bar{\Delta} $	10.4	5.9	5.9	0.4	8.5	9.8	3.2
$ \Delta _{\text{max}}$	16.4	12.8	8.6	1.3	14.3	16.2	5.5

models perform no better, overestimating the polarizabilities by 8–9%. The difference between LDA and BLYP polarizabilities is very small. Clearly, the gradient correction introduced at the BLYP level has little effect on the polarizabilities (and indeed in the wrong direction). The irrelevance of the gradient correction for polarizabilities may be understood from the fact that most of the contributions to the polarizabilities arise from the outer region of the electronic structure, where

the density gradient is small. Clearly, the assumptions underlying the ALDA model are well founded.

As some proportion of exact exchange is introduced at the B3LYP level, we observe a striking improvement in the performance of DFT—the mean absolute B3LYP error is 3.2%, significantly smaller than the CCS and CC2 mean absolute errors of 5.9%. Although only three molecules are investigated here, it appears that the non-local description of exchange at the B3LYP level

Table 9. The first hyperpolarizability tensor (atomic units) of HF in the t-aug-cc-pVTZ basis, with the z axis as the symmetry axis. The coupled-cluster values have been taken from [17].

	λ	HF	CCS	CC2	CCSD	CC3	LDA	BLYP	B3LYP	
SHG	zzz	∞	-8.40	-10.04	-12.28	-9.84	-9.44	-10.65	-10.83	-9.80
	zxx	∞	-0.51	-1.00	-2.79	-1.69	-1.52	-2.29	-1.99	-1.43
	xzx	∞	-0.51	-1.00	-2.79	-1.69	-1.52	-2.29	-1.99	-1.43
	zzz	694.3 nm	-9.06	-10.74	-13.45	-10.70	-10.29	-11.88	-12.10	-10.82
		632.8 nm	-9.20	-10.89	-13.70	-10.89	-10.48	-12.15	-12.39	-11.05
	zxx	694.3 nm	-0.51	-1.00	-3.10	-1.82	-1.64	-2.58	-2.24	-1.56
OR	zxx	632.8 nm	-0.51	-1.00	-3.17	-1.85	-1.67	-2.65	-2.30	-1.58
	xzx	694.3 nm	-0.62	-1.15	-3.40	-2.05	-1.86	-3.03	-2.78	-1.89
		632.8 nm	-0.65	-1.18	-3.56	-2.14	-1.95	-3.23	-3.00	-2.01
	zzz	694.3 nm	-8.61	-10.26	-12.65	-10.12	-9.71	-11.04	-11.23	-10.13
		632.8 nm	-8.65	-10.31	-12.73	-10.17	-9.77	-11.12	-11.31	-10.19
	zxx	694.3 nm	-0.56	-1.06	-3.00	-1.82	-1.64	-2.54	-2.26	-1.59
OR	zxx	632.8 nm	-0.57	-1.07	-3.05	-1.85	-1.67	-2.60	-2.32	-1.63
	xzx	694.3 nm	-0.52	-1.02	-2.92	-1.75	-1.58	-2.42	-2.12	-1.50
		632.8 nm	-0.53	-1.02	-2.94	-1.77	-1.59	-2.45	-2.15	-1.52

Table 10. The first hyperpolarizability tensor (atomic units) of CO in the d-aug-cc-pVTZ basis, with the z axis as the symmetry axis. The coupled-cluster values have been taken from [18].

	λ	HF	CCS	CC2	CCSD	CC3	LDA	BLYP	B3LYP	
SHG	zzz	∞	31.42	35.65	26.34	28.39	28.79	33.53	32.95	31.70
	zxx	∞	5.12	3.79	6.33	6.99	8.23	8.91	8.70	7.51
	xzx	∞	5.12	3.79	6.33	6.99	8.23	8.91	8.70	7.51
	zzz	694.3 nm	35.41	39.73	30.69	32.68	33.42	39.57	39.01	36.93
		632.8 nm	36.32	40.66	31.71	33.68	34.50	41.02	40.48	38.18
	zxx	694.3 nm	6.54	5.10	8.17	8.91	10.45	11.71	11.54	9.81
OR	zxx	632.8 nm	6.88	5.42	8.61	9.38	10.98	12.41	12.25	10.38
	xzx	694.3 nm	5.43	3.73	7.17	7.98	9.60	10.75	10.68	8.86
		632.8 nm	5.49	3.71	7.37	8.22	9.94	11.22	11.20	9.19
	zzz	694.3 nm	32.66	36.93	27.69	29.72	30.21	35.37	34.78	33.30
		632.8 nm	32.93	37.20	27.97	30.00	30.52	35.76	35.18	33.64
	zxx	694.3 nm	5.11	3.64	6.48	7.20	8.56	9.34	9.17	7.81
OR	zxx	632.8 nm	5.11	3.61	6.52	7.24	8.63	9.44	9.28	7.87
	xzx	694.3 nm	5.45	4.05	6.78	7.48	8.82	9.65	9.45	8.10
		632.8 nm	5.52	4.11	6.88	7.59	8.94	9.81	9.61	8.23

may be important for the description of polarizabilities and similar properties. We finally note that, although the CCS and CC2 models give similar mean absolute errors of about 6%, the errors are in opposite directions. Thus, whereas the CCS model mostly underestimates the polarizabilities, they are overestimated by the CC2 model. This behaviour of the polarizabilities is in agreement with the differences observed between the CCS and CC2 excitation energies in section 3.1.

Finally, comparing the errors in table 4 and 8, we note the expected general correlation between an overestimation of excitation energies and an underestimation of polarizabilities by most of the wave-function models, and between an underestimation of excitation energies and an overestimation of polarizabilities by DFT. However, the CC2 model errs on the same side

as the DFT models, whereas the CCSD model tends to very slightly overestimate both excitation energies and polarizabilities.

3.3 The frequency-dependent hyperpolarizabilities of HF, CO, and H₂O

The Cartesian components of the first frequency-dependent hyperpolarizabilities β_{ijk} of HF, CO, and H₂O are listed in tables 9–11, with associated statistical measures of error collected in table 12. In addition, we have in table 13 listed the corresponding parallel components of the static hyperpolarizabilities

$$\beta_{\parallel} = \frac{1}{5} \sum_i (\beta_{iiz} + \beta_{izi} + \beta_{zii}), \quad (3)$$

Table 11. The first hyperpolarizability tensor (atomic units) of H₂O in the d-aug-cc-pVTZ basis, with the molecule in the *xz* plane and the *z* axis as the symmetry axis. The coupled-cluster values have been taken from [18].

	λ	HF	CCS	CC2	CCSD	CC3	LDA	BLYP	B3LYP	
SHG	<i>zzz</i>	∞	-7.29	-10.40	-20.66	-13.97	-13.20	-19.14	-18.61	-14.31
	<i>zxx</i>	∞	-1.24	-2.58	-9.32	-5.66	-5.33	-8.82	-8.22	-5.52
	<i>xxz</i>	∞	-1.24	-2.58	-9.32	-5.66	-5.33	-8.82	-8.22	-5.52
	<i>zyy</i>	∞	-9.35	-10.41	-12.04	-9.92	-9.88	-11.67	-12.59	-11.07
	<i>yyz</i>	∞	-9.35	-10.41	-12.04	-9.92	-9.88	-11.67	-12.59	-11.07
	<i>zzz</i>	694.3 nm	-8.58	-11.88	-25.50	-16.93	-16.13	-25.22	-24.96	-18.37
		632.8 nm	-8.88	-12.23	-26.71	-17.66	-16.58	-26.81	-26.66	-19.41
	<i>zxx</i>	694.3 nm	-1.27	-2.65	-11.55	-6.68	-6.36	-11.45	-10.78	-6.84
		632.8 nm	-1.27	-2.65	-12.09	-6.92	-6.60	-12.11	-11.41	-7.16
	<i>xxz</i>	694.3 nm	-2.03	-3.54	-14.12	-8.48	-8.10	-15.57	-15.98	-9.63
		632.8 nm	-2.25	-3.81	-15.59	-9.32	-8.93	-17.90	-18.87	-10.99
	<i>zyy</i>	694.3 nm	-10.54	-11.56	-14.19	-11.47	-11.48	-14.39	-15.70	-13.28
	632.8 nm	-10.81	-11.82	-14.71	-11.84	-11.87	-15.09	-16.51	-13.83	
<i>yyz</i>	694.3 nm	-10.50	-11.61	-13.90	-11.36	-11.33	-13.99	-15.25	-13.02	
	632.8 nm	-10.76	-11.88	-14.34	-11.69	-11.67	-14.56	-15.90	-13.49	
OR	<i>zzz</i>	694.3 nm	-7.68	-10.86	-22.10	-14.86	-14.08	-20.90	-20.42	-15.49
		632.8 nm	-7.76	-10.95	-22.42	-15.05	-14.27	-21.28	-20.82	-15.75
	<i>zxx</i>	694.3 nm	-1.53	-2.93	-10.79	-6.56	-6.21	-10.77	-10.40	-6.76
		632.8 nm	-1.59	-3.01	-11.13	-6.77	-6.41	-11.24	-10.93	-7.06
	<i>xxz</i>	694.3 nm	-1.33	-2.69	-10.19	-6.12	-5.78	-9.89	-9.32	-6.13
		632.8 nm	-1.34	-2.71	-10.38	-6.22	-5.89	-10.13	-9.58	-6.27
	<i>zyy</i>	694.3 nm	-9.71	-10.80	-12.59	-10.36	-10.32	-12.34	-13.35	-11.65
		632.8 nm	-9.79	-10.88	-12.71	-10.45	-10.41	-12.48	-13.51	-11.77
	<i>yyz</i>	694.3 nm	-9.72	-10.78	-12.66	-10.39	-10.36	-12.43	-13.45	-11.71
		632.8 nm	-9.80	-10.85	-12.79	-10.48	-10.46	-12.60	-13.64	-11.84

Table 12. Statistics relative to CC3 (%) for all Cartesian components of the hyperpolarizabilities of HF, CO, and H₂O.

	HF	CCS	CC2	CCSD	LDA	BLYP	B3LYP
$\bar{\Delta}$	-39.1	-26.0	36.4	0.9	37.9	35.0	4.7
Δ_{std}	29.6	28.3	40.8	8.7	26.2	23.4	8.9
$ \bar{\Delta} $	40.5	31.9	46.4	6.9	37.9	35.0	8.9
$ \Delta _{\text{max}}$	80.8	62.7	89.8	17.3	100.0	111.0	23.1

together with the parallel components of the second-harmonic generation (SHG) and optical-rectification (OR) hyperpolarizabilities

$$\beta_{\parallel}^{\text{SHG}} = \beta_{\parallel}(-2\omega, \omega, \omega), \quad (4)$$

$$\beta_{\parallel}^{\text{OR}} = \beta_{\parallel}(0, \omega, -\omega). \quad (5)$$

Finally, table 13 also contains statistical measures of error for the parallel components of the hyperpolarizabilities.

As for the polarizabilities in section 3.2, we here use the CC3 values as benchmarks. We note, however, that the CC3 errors are likely to be larger for the hyperpolarizabilities than for the polarizabilities. Thus, from

table 12, we see that, relative to CC3, the mean and maximum absolute errors in the CCSD hyperpolarizabilities are 9% and 17%, respectively. Since the corresponding Hartree-Fock errors relative to CC3 are 41% and 81%, respectively, we may assume that the CC3 hyperpolarizabilities are in error by about 1% relative to the corresponding FCI result, with a maximum error of perhaps 3%. Basis-set errors are also larger than for the polarizabilities (2–3%) but are probably less important than the intrinsic CC3 error since, from [18], it appears that most of the basis-set error is related to the description of the polarization rather than correlation. Since these errors are similar for DFT and coupled-cluster theory, they should not affect our comparison of the different models strongly,

Table 13. Parallel components of the first hyperpolarizability (atomic units) of HF (t-aug-cc-pVTZ), and CO and H₂O (d-aug-cc-pVTZ).

	λ	HF	CCS ^a	CC2 ^a	CCSD ^a	CC3 ^b	LDA	BLYP	B3LYP	Exp.	
HF	∞	-5.65	-7.22	-10.72	-7.93	-7.48	-9.14	-8.89	-7.60		
	SHG	694.3 nm	-6.14	-7.76	-12.03	-8.79	-8.32	-10.58	-10.38	-8.63	-9.9 ± 1.0^c
		632.8 nm	-6.24	-7.88	-12.34	-8.99	-8.51	-10.93	-10.75	-8.87	
	OR	694.3 nm	-5.81	-7.39	-11.12	-8.20	-7.75	-9.58	-9.34	-7.91	
632.8 nm		-5.84	-7.43	-11.21	-8.26	-7.80	-9.67	-9.43	-7.98		
CO	∞	25.00	25.94	23.40	25.42	27.15	30.81	30.21	28.03		
	SHG	694.3 nm	28.21	28.86	27.42	29.56	31.91	37.03	36.57	33.16	30.2 ± 3.2^d
		632.8 nm	28.94	29.53	28.37	30.54	33.04	38.55	38.15	34.41	
	OR	694.3 nm	26.01	26.85	24.63	26.70	28.61	32.68	32.10	29.58	
632.8 nm		26.22	27.05	24.89	26.97	28.92	33.08	32.51	29.92		
H ₂ O	∞	-10.73	-14.03	-25.21	-17.73	-17.05	-23.78	-23.65	-18.54		
	SHG	694.3 nm	-12.52	-16.03	-31.66	-21.72	-21.02	-32.12	-32.76	-24.11	-20.9 ± 1^e
		632.8 nm	-12.95	-16.51	-33.36	-22.75	-21.88	-34.51	-35.49	-25.64	
	OR	694.3 nm	-11.27	-14.65	-27.08	-18.90	-18.21	-26.09	-26.11	-20.11	
632.8 nm		-11.39	-14.77	-27.49	-19.15	-18.47	-26.60	-26.67	-20.46		
$\bar{\Delta}$		-24.8	-11.3	26.6	0.9	0.0	29.2	28.1	6.3		
Δ_{std}		12.3	7.6	29.8	5.8	0.0	14.7	16.6	4.9		
$ \bar{\Delta} $		24.8	11.3	35.9	5.5	0.0	29.2	28.1	6.3		
$ \Delta _{\text{max}}$		40.8	24.5	52.5	7.6	0.0	57.7	62.2	17.2		

^aCCS, CC2, and CCSD results for HF from [30] and for CO and H₂O from [18].

^bCC3 results for HF from [30] and for CO and H₂O from [17].

^cEquilibrium value based on experimental measurement of -10.9 ± 0.95 a.u. of Dudley and Ward [31], vibrational averaging of -0.65 a.u. from CASSCF calculations in [32], and a purely vibrational contribution of -0.35 a.u. from [33]. See also [17].

^dExperimental measurement from [34, 35]. No vibrational zero-point corrections and pure vibrational contributions are available—see [18].

^eEquilibrium value based on experimental measurement of -22.0 ± 0.9 a.u. [34, 35], vibrational averaging of -1.83 a.u. [36], and a purely vibrational contribution of -0.21 a.u. [37]. See also the discussion in [18].

recalling that all calculations have been carried out in the same one-electron basis (t-aug-cc-pVTZ for HF and d-aug-cc-pVTZ for CO and H₂O).

As for polarizabilities, we find that the LDA and BLYP functionals perform in a very similar manner, giving almost as large mean absolute errors as the Hartree–Fock method but in the opposite direction. Thus, whereas the mean error of the Hartree–Fock method is -39% , they are 38% and 35% for the LDA and BLYP functionals, respectively. Again, the B3LYP functional represents a significant improvement on the Hartree–Fock method, with mean and mean absolute errors of 4.7% and 8.9% , respectively. In fact, the B3LYP model compares well with the CCSD model, which has mean and mean absolute errors of 0.9% and 6.9% , respectively. The B3LYP performance is particularly impressive relative to the CCS and CC2 models, which have mean errors as large as -26% and 36% , respectively.

Comparing the errors in tables 8 and 12, we note that the performance of the different methods for the hyperpolarizabilities is a reflection of their performance for the polarizabilities. In particular, the hyperpolarizabilities are underestimated by the same models that

underestimate the polarizabilities—that is, by the Hartree–Fock and CCS models. In general, however, the errors are much larger for the hyperpolarizabilities than for the polarizabilities, the only exception being the B3LYP method, which performs no worse for hyperpolarizabilities than it does for polarizabilities. Since our analysis is based on only three molecules, we cannot rule out the possibility that this excellent performance of the B3LYP model is accidental rather than typical.

3.4 Dispersion of the polarizabilities and hyperpolarizabilities

Expanding the isotropic polarizability and parallel component of the hyperpolarizability tensors in even powers of the frequency ω , we obtain

$$\alpha(\omega) = \alpha(0)[1 + 6\omega^2 A + \mathcal{O}(\omega^4)], \quad (6)$$

$$\beta_{\parallel}(\omega) = \beta_{\parallel}(0)[1 + 6\omega^2 A + \mathcal{O}(\omega^4)], \quad (7)$$

where the expansion coefficient A may be determined by a least-squares fitting to $\alpha(\omega)$ and $\beta_{\parallel}(\omega)$, calculated at different frequencies ω . In table 14, we have listed the coefficients obtained by fitting the calculated

Table 14. The dispersion coefficients (atomic units) for the polarizability and the SHG and OR hyperpolarizabilities of HF in the t-aug-cc-pVTZ basis and of CO and H₂O in the d-aug-cc-pVTZ basis. The statistical measures of error (%) are given relative to the CC3 results.

		HF	CCS	CC2	CCSD	CC3	LDA	BLYP	B3LYP
α	HF	0.11	0.24	0.18	0.35	0.47	0.66	0.40	0.19
	CO	0.58	0.49	0.69	0.48	0.53	0.77	0.60	0.75
	H ₂ O	0.55	0.26	0.71	0.54	0.61	0.59	0.66	0.73
SHG	HF	3.35	2.68	4.10	3.71	3.95	5.12	5.31	4.62
	CO	4.49	3.90	5.77	5.46	5.86	6.52	6.67	5.93
	H ₂ O	5.50	4.70	7.49	6.78	8.54	9.00	9.08	8.27
OR	HF	1.17	0.79	1.32	1.22	1.50	1.86	1.99	1.44
	CO	1.54	1.27	1.97	1.89	2.01	2.25	2.29	2.00
	H ₂ O	1.80	1.78	2.69	2.45	2.41	3.50	3.63	3.02
$\bar{\Delta}$		-24.9	-37.1	-3.2	-11.7	0.0	22.9	17.2	4.0
Δ_{std}		23.0	14.6	25.8	8.8	0.0	17.6	19.5	28.7
$ \bar{\Delta} $		26.9	37.1	16.7	12.1	0.0	23.6	20.9	19.2
$ \Delta _{\text{max}}$		76.5	57.2	61.8	26.6	0.0	44.9	50.5	60.8

polarizabilities and hyperpolarizabilities of HF, CO, and H₂O (in the static limit and for wavelengths 694.3 and 632.8 nm) to polynomials of the general form $a + b\omega^2 + c\omega^4$. Since the frequencies used here are not optimal for the calculation of dispersion coefficients, there is an uncertainty in the last digit quoted in the table.

As expected, the dispersion is larger for the hyperpolarizability—in particular, for $\beta_{\parallel}^{\text{SHG}}$ —than for the polarizability. We note a clear tendency for DFT to overestimate the dispersion, in particular for the pure LDA and BLYP functionals. Somewhat surprisingly, the B3LYP functional provides a better representation of the dispersion of the hyperpolarizabilities than of the polarizability, strongly underestimating the polarizability dispersion of HF but overestimating the polarizability dispersion of CO and H₂O. The wave-function models behave differently from DFT, underestimating rather than overestimating the dispersion—in particular, at the CCS level of theory. This difference is not surprising in view of the tendency of the wave-function models to overestimate excitation energies and the tendency of DFT to underestimate these energies.

3.5 The hyperpolarizability of para-nitroaniline

Having compared DFT with accurate coupled-cluster calculations for small molecules, we now turn our attention to a much larger system—that is, the PNA molecule, which has served as an important test system for experimental and theoretical studies of hyperpolarizabilities. Of particular interest here is the parallel component of the SHG hyperpolarizability tensor

$$\beta_z^{\text{SHG}}(\omega) = \sum_k (\beta_{zkk} + \beta_{kzk} + \beta_{kkz}), \quad (8)$$

where z is the molecular C_{2v} symmetry axis. Early Hartree–Fock and π -electron multi-configurational self-consistent field (MCSCF) quadratic-response calculations by Luo *et al.* [28] gave 5.7 and 8.2×10^{-30} esu, respectively, for this component at 1.17 eV, which is much too low compared with the experimental value of 16.9×10^{-30} esu, as extrapolated from solvent measurements at the same frequency [29]. These discrepancies were first attributed to solvation, but subsequent gas-phase measurements yielded a similar value of 15.4×10^{-30} esu, confirming previous measurements and pointing to serious deficiencies in the computational models. Recently, Sałek *et al.* calculated the hyperpolarizability of PNA at the B3LYP level of theory, obtaining the values listed in table 15, along with previous calculations and measurements of $\beta_z^{\text{SHG}}(\omega)$ in PNA [7].

At low frequencies, the agreement of the B3LYP values with experiment is reasonable. Thus, at 1.17 eV, the B3LYP model gives 12.9×10^{-30} esu, which is 16% lower than the experimental result. At higher frequencies, however, the B3LYP values are in much poorer agreement with experiment, underestimating the experimental values by 30% at 1.364 eV and by more than 40% at 1.494 eV (see table 15), indicating problems also with the B3LYP model. However, in view of the large uncertainties in the experimental values and the fact that they were obtained by extrapolation from solvent measurements, these discrepancies may also arise from problems with the experimental measurements at high frequencies. In the present paper, we have therefore re-investigated this problem, carrying out calculations of $\beta_z^{\text{SHG}}(\omega)$ at the CCSD level of theory.

In table 16, we have collected the results of CCSD calculations of the first hyperpolarizability components of PNA at different frequencies, comparing with the corresponding results obtained with the B3LYP model.

Table 15. The hyperpolarizability $\beta_z^{\text{SHG}}(\omega)$ average of PNA in units of 10^{-30} esu (1 a.u. = 8.639418×10^{-33} esu), using the B-convention.

ω (eV)	0	0.65	1.17	1.364	1.494
RHF ^a	4.09	4.50	5.68	6.50	7.24
MCSCF ^a	5.93	6.52	8.20	9.38	10.43
MP2 ^b			12.0		
LDA/ALDA ^c			16.99		
LB94/ALDA ^c			21.16		
B3LYP ^d	6.72	7.94	12.33	16.28	21.16
B3LYP ^e	6.85	8.15	12.94	17.41	23.09
CCSD ^f	5.82		8.47		
CCSD ^g	7.50	8.24	11.52	13.83	16.12
CCSD ^h	7.38		11.37		
Exp. ⁱ		9.6 ± 0.5	16.9 ± 0.4	25.0 ± 1	40.0 ± 3
Exp. ^j			15.44 ± 0.63		

^aFrom [28].^bFrom [38] using RPA dispersion.^cFrom [39].^dFrom [7] using the aug-cc-pVDZ basis.^eFrom [7] using the Sadlej basis.^fPresent results using the cc-pVDZ basis.^gPresent results using the aug-cc-pVDZ basis.^hPresent results using a stripped down aug-cc-pVTZ basis.ⁱExperiment from [29] extrapolated from solvent measurements.^jExperiment from [40] in the gas phase.Table 16. CCSD and B3LYP results for the β components of PNA in units of 10^{-30} esu (1 a.u. = 8.639418×10^{-33} esu), with the phenyl ring in the xz plane and the z axis as the C_{2v} symmetry axis.

ω (eV)	CCSD		B3LYP		
	aug-cc-pVDZ	cc-pVDZ	aug-cc-pVDZ	Sadlej	
zxx	0	-1.05	-1.36	-1.22	-1.10
	0.650	-1.13	-1.49	-1.36	-1.21
	1.170	-1.36	-1.90	-1.82	-1.60
	1.361	-1.53	-2.24	-2.23	-1.95
	1.494	-1.69	-2.63	-2.73	-2.39
zyy	0	-0.53	-0.08	-0.58	-0.59
	0.650	-0.56	-0.08	-0.62	-0.63
	1.170	-0.65	-0.10	-0.76	-0.78
	1.361	-0.70	-0.11	-0.87	-0.90
	1.494	-0.76	-0.13	-0.10	-1.04
xxz	0	-1.05	-1.36	-1.22	-1.10
	0.650	-1.08	-1.41	-1.27	-1.14
	1.170	-1.16	-1.52	-1.41	-1.24
	1.361	-1.19	-1.59	-1.49	-1.30
	1.494	-1.23	-1.65	-1.56	-1.35
yyz	0	-0.53	-0.08	-0.58	-0.59
	0.650	-0.56	-0.08	-0.62	-0.63
	1.170	-0.64	-0.09	-0.71	-0.73
	1.361	-0.69	-0.09	-0.77	-0.80
	1.494	-0.73	-0.10	-0.83	-0.86
zzz	0	16.58	11.69	15.25	15.40
	0.650	18.61	13.47	17.80	18.11
	1.170	24.90	19.47	26.93	28.00
	1.361	29.65	24.41	35.10	37.16
	1.494	34.38	30.03	45.16	48.81

Comparing the CCSD and B3LYP results in the aug-cc-pVDZ basis, we note a clear tendency of the B3LYP model to give hyperpolarizabilities that are larger than those obtained with the CCSD model—in particular, at high frequencies. Indeed, these observations are in agreement with our benchmark calculations on the hyperpolarizabilities of small molecules in section 3.3 and their dispersion in section 3.4. We do note, however, that an exception to this rule occurs for the dominant β_{zzz} component at the two lowest frequencies. These results therefore indicate that the underestimation of the experimental hyperpolarizability of PNA by B3LYP may arise from experimental errors rather than from problems with the calculations. Another possible explanation of the discrepancy between theory and experiment is a probable red-shift of the lowest transition in solution, altering the slope of the dispersion curve. It is quite possible that the higher frequencies are close to a resonance frequency in solution (experiment) but a bit further away in vacuum (theory). The cited experimental results are corrected for solvation effects, but the correction is expected to be of lower quality close to a resonance.

In table 15, we have listed the values of $\beta_z^{\text{SHG}}(\omega)$ calculated using the CCSD model with different basis sets, including the stripped down aug-cc-pVTZ basis. At 1.17 eV, the CCSD model gives a value of 11.4×10^{-30} esu, somewhat lower than the B3LYP result of 12.9×10^{-30} esu and much lower than the experimental value of 15.4×10^{-30} esu. Since, at higher frequencies, the discrepancy between the B3LYP and CCSD models increases even more, it appears that the very large differences observed between the experimental measurements and the B3LYP values must arise from problems with the experimental measurements rather than with the calculations. In fact, from a comparison of the B3LYP and CCSD results, it appears that the problem with the B3LYP model is an overestimation rather than an underestimation of the hyperpolarizabilities at high frequencies.

4. Conclusions

We have compared the lowest singlet excitation energies, frequency-dependent polarizabilities, and the frequency-dependent first hyperpolarizabilities of HF, CO, and H₂O calculated by means of coupled-cluster theory (Hartree–Fock, CCS, CC2, CCSD, and CC3) and DFT (LDA, BLYP, and B3LYP), at the same geometries and in the same basis sets. All DFT methods (LDA, BLYP, and B3LYP) tend to underestimate excitation energies and overestimate polarizabilities and hyperpolarizabilities, in contrast to the Hartree–Fock and CCS methods,

which overestimate excitation energies and underestimate polarizabilities by approximately the same amount. The CC2 and CCSD methods usually give errors relative to CC3 that are in the same direction as those observed with DFT.

Of all methods investigated, the CCSD method gives results closest to the CC3 method, with mean absolute errors of 1% for excitation energies, 0.4% for polarizabilities, and 7% for hyperpolarizabilities. Except for the hyperpolarizabilities, this accuracy is about an order of magnitude better than that of the Hartree–Fock method, which has mean absolute errors of 10% for excitation energies, 10% for polarizabilities, and 41% for hyperpolarizabilities. The corresponding CCS and CC2 mean absolute errors are 10% and 5%, respectively, for excitation energies, 6% (both methods) for polarizabilities, and 32% and 46%, respectively, for hyperpolarizabilities. Thus, whereas the CC2 method represents a significant improvement on Hartree–Fock theory for excitation energies and polarizabilities, it performs poorly for first hyperpolarizabilities.

Concerning the DFT methods, we first note that the LDA and BLYP methods behave in a very similar manner, with mean absolute errors of 18% and 20%, respectively, for excitation energies, 9% and 10% for polarizabilities, and 38% and 35% for first hyperpolarizabilities. Thus, whereas the LDA and BLYP methods perform very poorly for excitation energies with errors about twice as large as those obtained at the Hartree–Fock level (and in the opposite direction), they perform slightly better than the Hartree–Fock method for polarizabilities and hyperpolarizabilities.

The hybrid B3LYP method represents a significant improvement on the pure DFT methods, with mean absolute errors of 12% for excitation energies, 3% for polarizabilities, and 9% for hyperpolarizabilities. The performance of B3LYP for hyperpolarizabilities is particularly impressive, approaching that of the CCSD method. Clearly, more thorough investigations are needed to establish whether this performance is typical rather than accidental. We note, however, that, since the Hartree–Fock and BLYP methods give errors of roughly similar magnitudes but in opposite directions, the improved performance of the B3LYP functional relative to the BLYP functional is not surprising.

In general, dispersion coefficients are underestimated by the wave-function methods and overestimated by DFT, in particular at the LDA and BLYP levels of theory. The B3LYP method performs slightly better than the LDA and BLYP methods but somewhat erratically.

Our calculations on the PNA molecule have established that, for this important molecule with a strong charge-transfer character, B3LYP performs reasonably

well but not excellently, underestimating the hyperpolarizability at low frequencies and underestimating it at high frequencies. At high frequencies, the CCSD and B3LYP results both disagree strongly with experiment, indicating the presence of a systematic error in the experimental results.

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