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Chemical Physics Letters 391 (2004) 27–32
CHEMICAL PHYSICS LETTERS
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The hyperpolarizability of the Ne atom in the approximate coupled cluster triples model CC3

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Received 7 April 2004; in final form 16 April 2004
Available online 18 May 2004

Abstract

The static and frequency-dependent hyperpolarizability of Ne is calculated using the coupled cluster approximate triples model CC3 and a large correlation-consistent basis set. Relativisitic contributions are taken into account through first-order. Analyzing in details the one- and N-electron errors, the uncertainty of the results is estimated to be about one atomic unit, an accuracy which for the first time is obtained for a many electron system in ab initio calculations of frequency-dependent second hyperpolarizabilities. For the static hyperpolarizability of Ne we obtain a best theoretical estimate of 107.6 ± 1.0 a.u. The frequency-dependent hyperpolarizability of Ne is also calculated at the lower levels of the coupled cluster hierarchy – CCS, CC2, and CCSD – and compared to CC3 to illustrate the importance of the inclusion of the triple excitations in coupled cluster wavefunctions for an accurate determination of hyperpolarizabilities. The results at the CC3 level agree well with the latest experimental results.
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1. Introduction

The accurate determination of the hyperpolarizability of atoms and molecules is a challenge for both theory and experiment. Significant progress has been made during the last 15–20 years both on the experimental and theoretical side. The interplay between theory and experiment has played an important role for this development; experimental progress has been followed by new theoretical developments and so on. The history of the hyperpolarizability of the Ne atom demonstrates the status of the field and puts the developments into some perspective. Even for this very simple atom there exists some uncertainty about the value of the static hyperpolarizability. Also the dispersion of the hyperpolarizability of Ne has been the subject of some controversy.

The history for the static hyperpolarizability is summarized in Table 1 and Fig. 1. The hyperpolarizability of Ne was first measured by Buckingham and Dunmur [1] in a Kerr experiment at 633 nm to 101 ± 8 a.u. The static hyperpolarizability was estimated to 98 ± 8 a.u. In a sequence of publications Shelton et al. [2–5] reported electric field-induced second harmonic generation (ESHG) experiments at different frequencies. Extrapolations to zero frequency resulted in a wide range of static hyperpolarizability values, as seen from Table 1. When a new experimental value was reported it was in several cases followed by a calculation which gave a hyperpolarizability in the same region. The experimental static hyperpolarizability of Shelton of 115.8 a.u. (1989) [3] and of 119 ± 3 a.u. (1990) [4] was based on ESHG experiments that showed an anomalous dispersion for the hyperpolarizability. The negative dispersion was challenged based on theoretical arguments and calculations by Bishop [6] and Jensen et al. [7], the latter carried out complete active space (CAS) calculations of the frequency-dependent hyperpolarizability and estimated the static hyperpolarizability to 99 ± 6 a.u. The discussion about the anomalous dispersion was settled in 1992 when Shelton [5] published new ESHG experiments and concluded that the dispersion was not anomalous and estimated the static hyperpolarizability to 108 ± 2 a.u. Christiansen and Jørgensen [8] reported in 1993 a static

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doi:10.1016/j.cplett.2004.04.055

Table 1
The history of the experiments and calculations on the static second hyperpolarizability of Ne

Year	Value (a.u.)	Method	Reference
Experiment			
1968	98 ± 8	Kerr	[1]
1988	84.0 ± 9	ESHG	[2]
1989	115.8	ESHG	[3]
1990	119 ± 3	ESHG	[4]
1992	108 ± 2	ESHG	[5]
1998	106 ± 2	Revised fit to ESHG	[9]
Calculations			
1986	104.6	MBPT4	[34]
1989	86.5	MCSCF	[10]
1989	119 ± 4	CCSD(T)	[11]
1991	99 ± 6	CAS MCSCF	[7]
1992	111 ± 4	CCSD(T)	[35]
1993	106 ± 5	RAS MCSCF	[8]
1994	107.3	CCSD(T)	[17]
1998	107.1 ± 3.0	CCSD(T)	[18]
2001	109.2 ± 1.4	CCSD(T)-R12+rel	[12]
2004	107.6 ± 1.0	CC3	This work

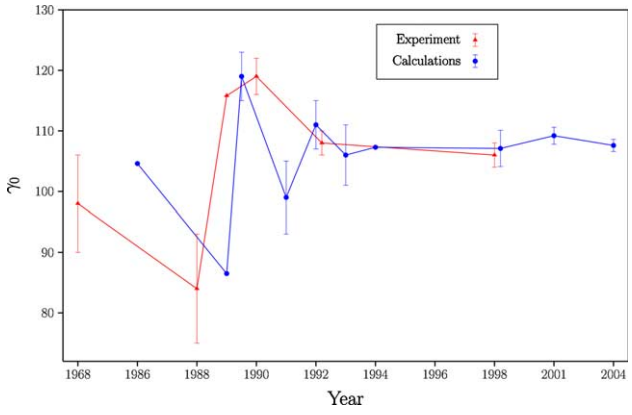


Fig. 1. The history of the experimental and theoretical determination of the static hyperpolarizability γ_0 (a.u.) for Ne atom.

hyperpolarizability of 106 ± 5 a.u. based on restricted active space (RAS) MCSCF calculations. More recent values for the static hyperpolarizability tend to be in the region of 106 ± 2 a.u. which Hättig and Jørgensen [9] proposed as the best experimental value based on a detailed analysis of Shelton's ESHG experiments and a revised fit for the experimental ESHG result. Retrospectively, it can be recognized that: the experimental results of [2–4] did not have the assumed quality to sustain the reported static hyperpolarizability values; the calculation in [10] did not use a basis that was large enough to give a proper description of the hyperpolarizability; the calculated value in [11] was based on numerical differentiation where the total energies were determined with too low accuracy; too much confidence was given in [7] to the accuracy that could be obtained using CAS wavefunctions; and that in [12] the relativistic effect was calculated to be much too large.

Even though theory and experiment has reached some consensus about the value of the static hyperpolarizability of Ne, there still exists an uncertainty of several per cent with respect to its actual value [9]. The goal of this Letter is to reduce this uncertainty. We do this by carrying out calculations of the hyperpolarizability using the coupled cluster hierarchy CCS, CC2 [13], CCSD, CC3 [14] ... which is designed to systematically improve the description of molecular response properties for a single configuration dominated system. In CCS all single excitations are treated, in CCSD all doubles are added and in CCSD(T) all triples are further added. CC2 and CC3 are approximations to CCSD and CCSDT where the doubles and the triples respectively are treated in an approximate fashion and where the scaling of CCSD and CCSDT is reduced.

We report here the first calculations of the frequency-dependent hyperpolarizability with the CC3 model. In CC3 triple exictations are accounted for in an approximate way, similar as in CCSD(T), but in an iterative fashion, which makes this model also suited for frequency-dependent properties. For many molecular properties the effect of triples is extremely important, for example for equilibrium geometries and atomization energies a statistical investigation on 18 molecules showed that the mean absolute error in CCSD decreased when triples were considered in an approximate fashion using CCSD(T) from 0.67 to 0.09 pm for equilibrium bond length [15] and from 32.2 to 4.1 kJ/mol for atomization energies [16]. The static hyperpolarizability of Ne has also been calculated using the CCSD(T) model and close agreement with the experimental static hyperpolarizability has been obtained, see for example [17,12]. The most accurate CCSD(T) result has been obtained in [18], where a triple augmented core-valence basis with cardinal number equal 5 (t-aug-cc-pCV5Z basis) was used. The CC3 model can be used to calculate both static and frequency-dependent hyperpolarizabilities. We expect similar reductions in the errors from CCSD to CC3 for the static and frequency-dependent hyperpolarizabilities of Ne as observed when going from CCSD to CCSD(T).

2. Computational details

Most ESHG experiments measure the isotropic average component $\gamma_{\parallel}^{\mathrm{ESHG}}(\omega)$ [19] which for atoms becomes

$$\gamma_{\parallel}^{\mathrm{ESHG}}(\omega) = \gamma_{zzzz}(-2\omega;\omega,\omega,0). \tag{1}$$

Static and frequency-dependent hyperpolarizabilities of Ne will be reported using the CCS, CC2, CCSD and CC3 coupled cluster models and Dunning's correlation-consistent basis sets cc-pVXZ augmented with diffuse functions [20]. We consider cardinal numbers X = D, T,

Q, 5, 6 and double (d), triple (t), and quadruple (q) augmentation. To investigate remaining basis set errors, in addition some SCF calculations in these and a large uncontracted basis (see below) and numerical Hartree–Fock calculations were carried out for the static limit of $\gamma_{\|}$. All basis set calculations were done with the DALTON program [21]. The implementation of analytic second hyperpolarizabilities for CC2 and CCSD has been described in [22] and the implementation for (MC)SCF wavefunctions in [23]. CC3 hyperpolarizabilities have recently been implemented by us [24] in the coupled-cluster code [14,25] which is part of the DALTON package [21]. The numerical Hartree–Fock calculations for γ were done by combining the two dimensional Hartree–Fock program (2D HF) [26] with the finite field procedure. For the numerical solution of the SCF equations a grid with, respectively, 390 and 430 points for the coordinates v and μ was used and the parameter R_∞ was set to 50.0 (see [26] for details). The thresholds for the convergence of the orbital energies and the orbital norm were set to 10^{-12} and 10^{-14}, respectively.

3. Results

In Table 2 the CC3 static hyperpolarizability of Ne is given in all electron calculations using the augmented valence correlation-consistent basis sets. In accordance with the experience from CCSD hyperpolarizability calculations on Ne [18] the most smooth convergence is obtained using triply augmented basis sets. Doubly augmented basis sets do not contain sufficient diffuseness to even approach an approximately converged value for cardinal number $X = 6$, while the quadruply augmented sets significantly overshoot the hyperpolarizability at $X = T$ and then seem to approach very slowly the basis set limit from above.

To investigate the basis set convergence in more details, we start with analyzing the basis set convergence of $\gamma_{\|}(0)$ at the Hartree–Fock level – see Table 3. The SCF/t-aug-cc-pV6Z result for the static hyperpolarizability of 68.88 a.u. deviates still by as much as 0.4 a.u. from the numerical HF (NHF) value of 69.3 a.u. reported in [27]. Test calculations in the t-aug-cc-pwCVQZ and t-aug-cc-pwCV5Z basis sets [28] showed that also the addition of tight functions does not change the results substantially. This suggested that the numerical HF value from [27] might be a few tenth of an a.u. too large. Therefore, we re-investigated the numerical Hartree–Fock limit of $\gamma_{\|}(0)$ for Ne by combining the finite field procedure with accurate NHF calculations for the dipole moment. The second hyperpolarizability was obtained by fitting the field-dependent dipole moment for 125 field strengths between −0.02 and +0.02 a.u. to a polynomial which in addition to the polarizability and $\gamma_{\|}(0)$ also accounted for the two next higher-order terms. The results obtained this way are 2.3767467 a.u. for the polarizability, which is in excellent agreement with the value of 2.37674 from [27], and 68.8313 a.u. for the hyperpolarizability, which, however, is about 0.5 a.u. lower than the value given in [27]. This result is in considerable better agreement with the results of the basis set calculations listed in Table 3. To further check this value we carried out a SCF basis set calculation in a rather large uncontracted basis set, which was constructed as follows: we discarded from the t-aug-cc-pV6Z the g, h, and i functions, which do not contribute to $\gamma_{\|}$ at the SCF level, decontracted the s, p, d, and f shells and added a (3d2f) set of tight exponents taken from the core correlation part of the cc-pwCV5Z basis [28]. This basis – for convenience denoted as basis A – was further extended by

1. a primitive (18s12p10d8f) set with the exponents interpolated even tempered between the exponents of basis A,
2. a (2s2p1d2f) set of tight functions extrapolated even tempered from the largest exponents of basis A,
3. and a (1s1p1d1f) set of diffuse functions taken from the q-aug-cc-pV6Z basis.

The resulting uncontracted (40s28p23d21f) basis gives at the SCF level a polarizability of 2.3767468 a.u.– in perfect agreement with the numerical Hartree–Fock results – and a hyperpolarizability of 68.83128 a.u. which corroborates the above revised numerical Hartree–Fock results. We can thus conclude that for the t-aug-cc-pV6Z basis the remaining basis set error at SCF level is about 0.05 a.u.

To analyze the basis set convergence of the correlation contribution to the hyperpolarizability, we first note

Table 2
Convergence of the CC3 static ESHG hyperpolarizability γ_0 (a.u.) for neon in n-aug-cc-pVXZ basis-set family (all electrons correlated)

Cardinal number XZ	Augmentation level n		
	d	t	q
DZ	79.12	89.15	89.33
TZ	91.16	107.31	111.46
QZ	97.69	107.53	108.79
5Z	105.74	107.97	107.99
6Z	107.00	107.77	107.77

Table 3
Convergence of the SCF static ESHG hyperpolarizability γ_0 (a.u.) for neon in n-aug-cc-pVXZ basis-set family (no frozen core approximation)

Cardinal number XZ	Augmentation level n		
	d	t	q
DZ	49.29	53.22	53.27
TZ	57.27	66.54	68.85
QZ	62.03	67.80	68.50
5Z	67.53	68.64	68.66
6Z	68.57	68.88	68.88
Numerical HF	68.8313		

that at the 5Z and 6Z level the correlation contribution (obtained by subtracting SCF values in Table 3 from the corresponding CC3 values in Table 2) is the same for triple and quadruple augmentation and that the SCF contribution is close to convergence at 5Z and 6Z level (see Table 3). The correlation contribution to the hyperpolarizability may thus be expected to converge in the fashion similar to the correlation energy and the two-point linear extrapolation procedure of [29] may be applied to estimate the basis-set limit of the correlation contribution to the hyperpolarizability. The extrapolation procedure applied to 5Z and 6Z levels gives 38.14 a.u. as the basis-set limit of the correlation contribution. Adding this number to the numerical Hartree–Fock result we obtain at this stage the estimate of 107.0 ± 0.4 a.u. for the static hyperpolarizability of Ne. The uncertainty of 0.4 a.u. has been obtained by adding the 0.05 a.u. basis-set uncertainty of numerical Hartree–Fock (see above) to 0.34 a.u., which is the half of the difference between the extrapolated correlation contribution (38.14 a.u.) and the correlation contribution in t-aug-cc-pV6Z basis (38.83 a.u.).

The above analysis of the basis-set uncertainty has been based on the results of all electron calculations using valence basis sets. In principle, all electron calculations should be carried out using core-valence basis sets. However, very small changes occur in all electron calculations of hyperpolarizabilities whether valence or core-valence basis sets are used, in particular for the basis sets with larger cardinal numbers. For example, all electron CC3/t-aug-cc-pCVTZ, CC3/t-aug-cc-pCVQZ, and CC3/t-aug-cc-pCV5Z calculations of the static hyperpolarizability give 106.69, 107.32 and 107.86 a.u., respectively; thus the difference between core-valence and the corresponding valence basis set results (see Table 2) is reduced from 0.62 a.u. at TZ level to 0.21 a.u. at QZ level, and further to 0.11 a.u. at 5Z level.

The results we present in Tables 2 and 3 have been obtained from nonrelativistic calculations. The relativistic contribution to the hyperpolarizability has been calculated by Franke et al. [12] to 3.1 a.u. This value appears rather large and would increase significantly the deviation between the calculated and the experimental results. Nakajima and Hirao [30] using the third-order Douglas–Kroll method and CCSD(T) model with a basis set derived from the subset of the even-tempered type universal Gaussian primitive set (see [30] for details) obtained 0.6 a.u. as the relativistic contribution to the hyperpolarizability. A similar result (0.59 a.u.) has been obtained by Klopper [31] from CCSD(T)/q-aug-cc-pCV6Z calculations, where all the first-order relativistic correction terms were included in a perturbative manner. Adding the relativistic contribution to the value of 107.0 ± 0.4 a.u. obtained above, we estimate the static hyperpolarizability of Ne to 107.6 ± 0.4 a.u., the uncertainty of 0.4 a.u. accounting for basis set effects. We note that adding the relativistic contribution brings us back (within the quoted uncertainty) to the t-aug-cc-pV6Z value in Table 2, showing that the relativistic contribution and the remaining basis-set contribution for this basis apparently cancel each other.

In Fig. 2 we have plotted the frequency-dependent hyperpolarizability for the CCS, CC2, CCSD and CC3 models using the t-aug-cc-pV6Z basis set. The experimental results which Shelton in his latest publication [5] claims can be trusted are also given in Fig. 2. From Fig. 2 it is seen that the correlation contribution to the hyperpolarizability is large. The CCS model underestimates while the CC2 model overestimates the correlation contribution. As observed many times previously, the CCSD model is robust and gives results in quantitative good agreement with the experimental results. The agreement with the experimental values is improved significantly when the triples are considered in the CC3 model. Improvements of similar size are obtained for the static and frequency-dependent hyperpolarizability, see Table 4. In Table 4 we have additionally included the results denoted as CCSD(T)/CCSD. These are the results which Hättig and Jørgensen [18] obtained by multiplying the CCSD frequency-dependent hyperpolarizabilities by the factor

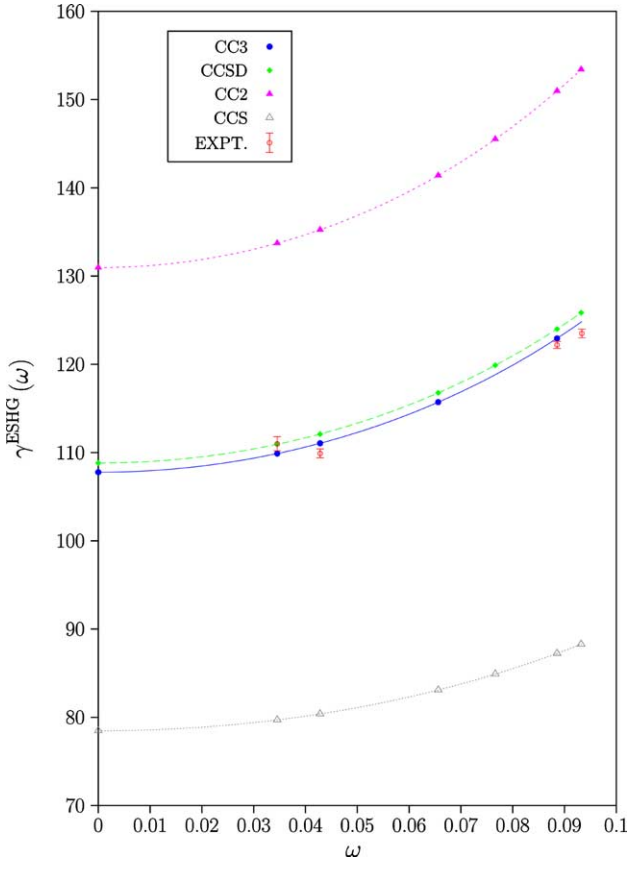


Fig. 2. Comparison of the second hyperpolarizability dispersion for Ne calculated with the various wavefunction approximations. The experimental ESHG results are also plotted. All numbers in a.u.

Table 4
Frequency-dependent second hyperpolarizability of Ne

Wave length	Freq.	CCS	CC2	CCSD	CC3	CCSD(T)/CCSD[a]	Exp.[b]
∞	0.000000	78.47	130.96	108.82	107.77	107.1	
1319	0.034544	79.70	133.72	110.93	109.89	109.2	111.0 ± 0.8
1064	0.042823	80.38	135.24	112.10	111.05	110.4	109.9 ± 0.5
694.3	0.065625	83.10	141.39	116.77	115.71	115.0	
594.5	0.076641	84.89	145.51	119.89			
514.5	0.088559	87.24	150.96	124.00	122.94	122.2	122.2 ± 0.4
488.8	0.093215	88.28	153.40	125.84			123.5 ± 0.5

The theoretical results have been obtained using t-aug-cc-pV6Z basis. Wave length in nm. All other numbers in a.u.
[a] The CCSD results multiplied by the factor $\gamma^{\mathrm{CCSD(T)}}_{\mathrm{t-aug-cc-pCV5Z}}(0)/\gamma^{\mathrm{CCSD}}_{\mathrm{t-aug-cc-pV5Z}}(0)$ to account approximately for core correlation and connected triples (see [18] for details).
[b] [5].

$\gamma^{\mathrm{CCSD(T)}}_{\mathrm{t-aug-cc-pCV5Z}}(0)/\ \gamma^{\mathrm{CCSD}}_{\mathrm{t-aug-cc-pV5Z}}(0)$ to account approximately for core correlation and connected triples. Comparing the CCSD(T)/CCSD frequency-dependent hyperpolarizabilities with the CC3 numbers, we conclude that the former constitute a good approximation to the frequency-dependent hyperpolarizabilities.

In Fig. 3 we have displayed only the CC3 hyperpolarizability and the experimental results. The agreement between the CC3 hyperpolarizability and the experimental results is significantly improved if the experimental hyperpolarizability at 1319 nm is ignored. Hättig and Jørgensen [9] have recommended to discard this value based on an analysis of the experimental results and a comparison with the dispersion of $\gamma_{\parallel}^{\mathrm{ESHG}}$ calculated at the CCSD level. The high accuracy of the CC3 hyperpolarizability and its dispersion sustain this recommendation. The errors of the CC3 results simply do not conform with the uncertainty given for the experimental hyperpolarizability at 1319 nm.

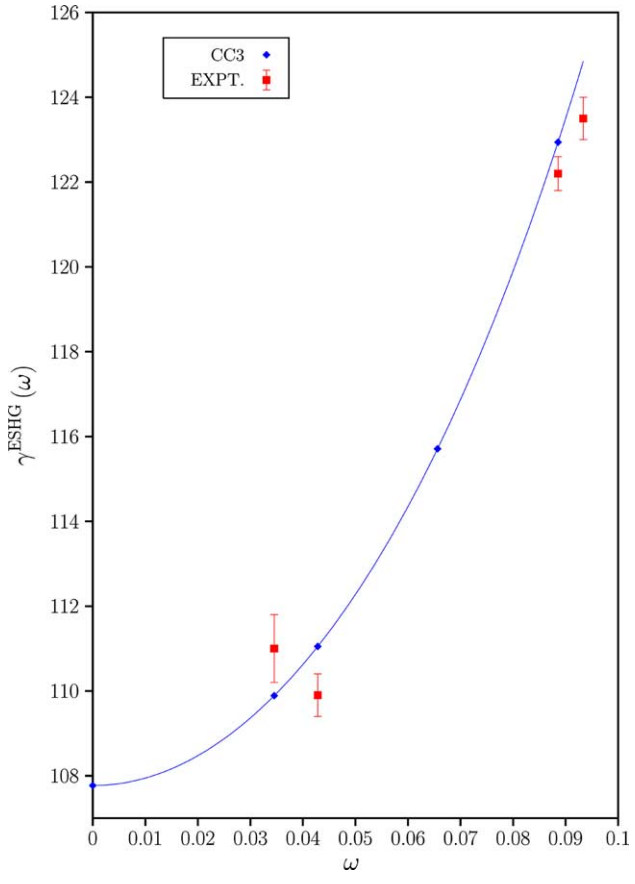


Fig. 3. The CC3 second hyperpolarizability dispersion for Ne compared to the experimental ESHG results. All numbers in a.u. The experimental numbers are: 111.0 ± 0.8 a.u. for $\omega = 1319$ nm, 109.9 ± 0.5 a.u. for $\omega = 1064$ nm, 122.2 ± 0.4 a.u. for $\omega = 514.5$ nm, and 123.5 ± 0.5 a.u. for $\omega = 488.0$ nm.

From Fig. 3 it is seen that the experimental results at 1064, 514.5, and 488.0 nm are between 0.5 and 1.0 a.u. lower than the CC3 values. As the basis-set error has been estimated above for CC3 to about 0.4 a.u. and the relativistic contribution has been found to approximately cancel out with the remaining basis-set contribution (which should hold both for static and frequency-dependent values), the deviation between the CC3 and the experimental results in Fig. 3 is mainly due to correlation effects beyond CC3. Comparison of CC3 and FCI polarizabilities and hyperpolarizabilities for HF, Ne, and BH [32] shows that the CC3 results have very small errors in these benchmark calculations; in fact, the errors in these benchmark calculations always were significantly smaller than one per cent. Larsen et al. [33] calculated the FCI static hyperpolarizability for Ne in aug-cc-pVDZ basis with frozen core to be 28.093 a.u. The CC3 calculations in the same basis (with frozen core) give the value of 28.049 a.u., which is 0.044 a.u. lower than the FCI result. This indicates that the CC3 hyperpolarizability is basically converged in N-electron space. Obviously, the aug-cc-pVDZ basis is too small to allow for definitive conclusions about the correlation error in CC3. The correlation error may alternatively be estimated comparing the static value of hyperpolarizability calculated, in a given basis, with CC3 and CCSD(T) models. The CC3 static hyperpolarizability for Ne in t-aug-cc-pCV5Z basis is 107.86 a.u., while the CCSD(T) gives in the same basis the value of 107.1 a.u. [18]. The CC3 correlation error may thus be estimated to

be less than one a.u. The correlation error will probably reduce the hyperpolarizability (the exact value is probably slightly overestimated by CC3), in line with the experimental results in Fig. 3.

We conclude that the CC3 hyperpolarizabilities of Ne, both static and frequency-dependent, calculated with sufficiently large basis (like t-aug-cc-pV6Z) and accounting for relativistic effects have an accuracy of about one atomic unit, the largest contribution to this uncertainty coming from the correlation effects beyond CC3. We thus obtain the best estimate of static hyperpolarizability of Ne as 107.6 ± 1.0 a.u.

Acknowledgements

We acknowledge the support from the European Research and Training Network: "Molecular Properties and Molecular Materials" (MOLPROP), contract No. HPRN-CT-2000-00013. This work was also partly supported by the Danish Natural Research Council (Grant No. 9901973). We also acknowledge the support from the Danish Center for Scientific Computing (DCSC).

References

[1] A.D. Buckingham, D.A. Dunmur, Trans. Faraday Soc. 64 (1968) 1776.
[2] D.P. Shelton, Z. Lu, Phys. Rev. A 37 (1988) 3813.
[3] D.P. Shelton, Phys. Rev. Lett. 62 (1989) 2660.
[4] D.P. Shelton, Phys. Rev. A 42 (1990) 2578.
[5] D.P. Shelton, E.A. Donley, Chem. Phys. Lett. 195 (1992) 591.
[6] D.M. Bishop, Phys. Rev. Lett. 65 (1990) 1688.
[7] H.J.Aa. Jensen, P. Jørgensen, H. Hettema, J. Olsen, Chem. Phys. Lett. 187 (1991) 387.
[8] O. Christiansen, P. Jørgensen, Chem. Phys. Lett. 207 (1993) 367.
[9] C. Hättig, P. Jørgensen, Chem. Phys. Lett. 283 (1998) 109.
[10] M. Jaszuński, D.L. Yeager, Phys. Rev. A 40 (1989) 1651.
[11] P.R. Taylor, T.J. Lee, J.E. Rice, J. Almlöf, Chem. Phys. Lett. 163 (1989) 359.
[12] R. Franke, H. Müller, J. Noga, J. Chem. Phys. 114 (2001) 7746.
[13] O. Christiansen, H. Koch, P. Jørgensen, Chem. Phys. Lett. 243 (1995) 409.
[14] H. Koch, O. Christiansen, P. Jørgensen, A.M. Sanchez de Merás, T. Helgaker, J. Chem. Phys. 106 (1997) 1808.
[15] K.L. Bak, P. Jørgensen, J. Olsen, T. Helgaker, W. Klopper, J. Chem. Phys. 112 (2000) 9229.
[16] K.L. Bak, J. Gauss, P. Jørgensen, J. Olsen, T. Helgaker, J.F. Stanton, J. Chem. Phys. 114 (2001) 6548.
[17] D.E. Woon, T.H. Dunning, J. Chem. Phys. 100 (1994) 2975.
[18] C. Hättig, P. Jørgensen, J. Chem. Phys. 109 (1998) 2762.
[19] D.P. Shelton, J.E. Rice, Chem. Rev. 94 (1994) 3.
[20] R.A. Kendall, T.H. Dunning Jr., R.J. Harrison, J. Chem. Phys. 96 (1992) 6769.
[21] T. Helgaker et al., DALTON, A Molecular Electronic Structure Program, Release 1.2, 2001.
[22] C. Hättig, O. Christiansen, P. Jørgensen, Chem. Phys. Lett. 282 (1998) 139.
[23] D. Jonsson, P. Norman, H. Ågren, J. Chem. Phys. 105 (1996) 6401.
[24] F. Pawłowski, P. Jørgensen, C. Hättig (to be published).
[25] K. Hald, P. Jørgensen, O. Christiansen, H. Koch, J. Chem. Phys. 116 (2002) 5963.
[26] J. Kobus, L. Laaksonen, D. Sundholm, Comp. Phys. Commun. 98 (1996) 346.
[27] J. Stiehler, J. Hinze, J. Phys. B 28 (1995) 4055.
[28] K.A. Peterson, T.H. Dunning, J. Chem. Phys. 117 (2002) 10 548.
[29] A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen, A.K. Wilson, Chem. Phys. Lett. 286 (1998) 243.
[30] T. Nakajima, K. Hirao, Chem. Lett. (2001) 766.
[31] Wim Klopper, Private communication.
[32] H. Larsen, J. Olsen, C. Hättig, P. Jørgensen, O. Christiansen, J. Gauss, J. Chem. Phys. 111 (1999) 1917.
[33] H. Larsen, J. Olsen, C. Hättig, Chem. Phys. Lett. 307 (1999) 235.
[34] I. Černušák, G.H. Dierksen, A.J. Sadlej, Phys. Rev. A 33 (1986) 814.
[35] P.R. Taylor, T.J. Lee, J.E. Rice, J. Almlöf, Chem. Phys. Lett. 189 (1992) 197.