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Basis set and electron correlation effects on the first and second static hyperpolarizability of SO₂

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Abstract

Accurate values are reported for the static hyperpolarizability of SO₂. We have obtained near-Hartree–Fock SCF values of $\mu_z = -0.7916 e a_0$ for the dipole moment, $\bar{\alpha} = 23.59$ and $\Delta\alpha = 11.73 e^2 a_0^2 E_h^{-1}$ for the mean and the anisotropy of the dipole polarizability, $\bar{\beta} = 35.0 e^3 a_0^3 E_h^{-2}$ for the mean first and $\bar{\gamma} = 2061 e^4 a_0^4 E_h^{-3}$ for the mean second dipole hyperpolarizability. Our CCSD(T) values for the electron correlation correction to these properties are $-0.1676 e a_0$, 2.25 and $1.38 e^2 a_0^2 E_h^{-1}$, $-4.8 e^3 a_0^3 E_h^{-2}$ and $1325 e^4 a_0^4 E_h^{-3}$. The mean $\bar{\beta} = 30.1 e^3 a_0^3 E_h^{-2}$ and $\bar{\gamma} = 3390 e^4 a_0^4 E_h^{-3}$ are larger than the experimental Kerr effect values at 632.8 nm. © 2000 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

Electric hyperpolarizability has come into prominence in late years because of its relevance to non-linear optics [1,2] and by extension to the design of novel NLO [3,4] materials. The property is also of importance from a general intermolecular interactions point of view [5] and relevant applications to refined molecular simulation studies have been reported [6]. Intense computational efforts are directed towards the accurate theoretical prediction of hyperpolarizabilities [7–9].

Very little is known about the electric hyperpolarizability of sulphur dioxide. A measurement of the electrooptical Kerr effect at 632.8 nm by Gentle et al. [10] resulted in mean first and second dipole hyperpolarizability estimates of $\bar{\beta} = 16 \pm 47 e^3 a_0^3$

E_h^{-2} and $\bar{\gamma} = 481 \pm 802 e^4 a_0^4 E_h^{-3}$. These values were found to be in poor agreement with the self-consistent field (SCF) values $\bar{\beta} = 32.9 e^3 a_0^3 E_h^{-2}$ and $\bar{\gamma} = 2038 e^4 a_0^4 E_h^{-3}$ reported by Maroulis [11]. The issue merits further investigation. In the case of SO₂, the hyperpolarizability makes only a small contribution to the measured Kerr constant and so the deduced estimates should not be considered as very accurate [10]. What is more, electron correlation effects are expected to change drastically the SCF picture of hyperpolarizability in small molecules [12,13]. In this Letter we examine in some depth two decisive factors: convergence to the Hartree–Fock limit and the size of electron correlation effects. Our approach to the calculation of electric hyperpolarizabilities relies on a finite-field scheme presented in detail in previous work [14]. The electric properties are extracted from calculations of the energy of the molecule perturbed by static homogeneous electric fields. We use large, carefully optimized basis sets of

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gaussian-type functions. The design of suitable basis sets for SO₂ constitutes an essential part of our endeavour.

2. Computational strategy

The energy of an uncharged molecule perturbed by a homogeneous electric field is easily expanded in terms of the field as [5]

$$E = E^0 - \mu_\alpha F_\alpha - (1/2) \alpha_{\alpha\beta} F_\alpha F_\beta - (1/6) \beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma - (1/24) \gamma_{\alpha\beta\gamma\delta} F_\alpha F_\beta F_\gamma F_\delta + \dots, \quad (1)$$

where the coefficients are the permanent dipole moment (μ_α), the dipole polarizability ($\alpha_{\alpha\beta}$), the first ($\beta_{\alpha\beta\gamma}$) and second ($\gamma_{\alpha\beta\gamma\delta}$) dipole hyperpolarizability. The independent components of these tensors for a molecule of C_{2v} symmetry, as SO₂, are one, three, three and six, respectively [5]. We follow a choice made in previous work [12]. In addition to the Cartesian components we also calculate the mean and the anisotropy of $\alpha_{\alpha\beta}$ and the mean of $\beta_{\alpha\beta\gamma}$ and $\gamma_{\alpha\beta\gamma\delta}$, defined as

$$\bar{\alpha} = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3, \quad (2a)$$

$$\Delta\alpha = (1/2)^{1/2} [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2]^{1/2}, \quad (2b)$$

$$\bar{\beta} = (3/5)(\beta_{zxx} + \beta_{zyy} + \beta_{zzz}), \quad (2c)$$

$$\bar{\gamma} = (1/5)(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{yyzz} + 2\gamma_{zzxx}). \quad (2d)$$

The expansion of Eq. (1) converges suitably fast for weak fields. A judicious choice of field strengths and directions allows the straightforward computation of all properties from the perturbed energies. Self-consistent field (SCF) and post-Hartree–Fock values are obtained in a uniform manner, as expanded elsewhere [14]. We use Møller–Plesset perturbation theory (MP) [15,16] and coupled-cluster techniques (CC) [17,18] for the calculation of electron correlation effects. The methods adopted are MP2 (second-order MP), MP4 (complete fourth-order MP) and SDQ-MP4, an inexpensive partial fourth-order approxima-

tion that excludes triple substitutions. Our most accurate values are obtained with CCSD (single and double excitation CC) and CCSD(T), which includes an estimate of connected triple excitations by a perturbational treatment. Last, a quantity of interest to our investigation is the total electron correlation correction (ECC), defined as

$$\text{ECC} = \text{CCSD(T)} - \text{SCF}. \quad (3)$$

3. Computational details

All basis used in this work have been especially designed for electric property calculations on SO₂. Their construction is part of a more general project to devise a computational strategy for the extension of theoretical studies to computationally demanding problems as collisional polarizability or the prediction of nonlinear optical properties of clusters. We have constructed seven basis sets using substrates (15s9p)[6s4p] and (11s6p)[5s3p] on S and O centres, respectively [19]. We follow a computational philosophy presented in some detail in previous work [12,14,20]. It consists of a systematic enlargement of the substrate by the addition, in three steps, of diffuse s- and p-GTF, tight d-GTF with exponents chosen to minimize E^0 and diffuse d-GTF with exponents chosen to maximize the mean dipole polarizability. This ensures that even the minimal [8s6p2d/7s5p2d] basis set, hereafter A0, yields a reliable description of the electric properties of the molecule. A0 consists of 100 CGTF and could be easily used for calculations on the (SO₂)₂ dimer or larger clusters. The remaining basis sets were obtained with the addition of more d- and f-GTF:

A0	(15s11p2d/13s8p2d)[8s6p2d/7s5p2d],	100CGTF
A1	(15s11p3d1f/13s8p3d1f)[8s6p3d1f/7s5p3d1f],	136CGTF
A2	(15s11p4d1f/13s8p3d1f)[8s6p4d1f/7s5p3d1f],	141CGTF
A3	(15s11p6d2f/13s8p4d1f)[8s6p6d2f/7s5p4d1f],	168CGTF
A4	(15s11p4d2f/13s8p4d2f)[8s6p4d2f/7s5p4d2f],	172CGTF
A5	(15s11p5d2f/13s8p4d2f)[8s6p5d2f/7s5p4d2f],	177CGTF
A6	(15s11p6d2f/13s8p4d2f)[8s6p6d2f/7s5p4d2f],	182CGTF

Even larger basis sets were employed in SCF calculations. Their construction follows the same method. From a (13s9p/12s7p)[6s5p/7s4p] initial basis set [21] we obtained K \equiv (16s11p6d3f/14s9p5d2f)[9s7p6d3f/9s6p5d2f], or 213 CGTF. Our largest ba-

Table 1

Convergence of SCF electric properties for SO₂

P	A0	A1	A2	A3	A4	A5	A6	K	P	D ^a
μ_z	−0.7987	−0.7974	−0.8009	−0.8039	−0.8125	−0.8022	−0.8022	−0.7916	−0.7916	−0.7877
α_{xx}	31.77	31.81	31.84	31.41	31.77	31.43	31.43	31.33	31.32	31.26
α_{yy}	18.52	18.57	18.59	18.61	18.60	18.63	18.62	18.66	18.66	18.64
α_{zz}	20.74	20.75	20.79	20.75	20.78	20.77	20.77	20.80	20.80	20.80
$\bar{\alpha}$	23.68	23.71	23.74	23.60	23.72	23.61	23.61	23.60	23.59	23.57
$\Delta\alpha$	12.29	12.29	12.31	11.88	12.22	11.88	11.88	11.75	11.73	11.69
β_{xxz}	23.6	23.8	23.1	23.3	24.0	23.4	23.4	23.0	23.0	22.0
β_{yyz}	6.4	7.0	7.1	6.4	6.9	6.6	6.5	6.7	6.6	6.4
β_{zzz}	27.2	28.2	28.0	28.3	28.0	28.9	28.6	28.8	28.7	26.5
$\bar{\beta}$	34.4	35.4	34.8	34.9	35.4	35.3	35.1	35.1	35.0	32.9
γ_{xxxx}	1825	2022	2045	2021	2035	2028	2030	2013	2014	1930
γ_{yyyy}	1377	1574	1552	1551	1538	1562	1561	1553	1560	1550
γ_{zzzz}	2406	2715	2748	2640	2740	2658	2663	2639	2637	2645
γ_{xxyy}	509	616	619	603	613	593	601	595	595	611
γ_{yyzz}	567	683	686	665	683	666	667	665	665	641
γ_{zzxx}	725	800	811	789	813	788	791	787	786	778
$\bar{\gamma}$	1842	2102	2116	2065	2108	2068	2075	2059	2061	2038

^a Basis set [8s6p5d1f/6s4p4d1f], 148 CGTF [11].

sis set is an uncontracted P \equiv (19s14p6d3f/15s10p5d2f) basis set, consisting of 280 GTF and built upon a (17s12p/13s8p) substrate [22,23]. Full details for all basis sets will be given elsewhere. 5D and 7F GTF were used in all calculations.

The seven innermost MP were kept frozen in all post-Hartree–Fock calculations.

The experimental geometry of $R_{\text{SO}} = 1.43076$ Å and $\angle(\text{O}–\text{S}–\text{O}) = 119.33^\circ$ was used in all calculations [24].

All calculations were performed with GAUSSIAN 94 [25].

Atomic units are used throughout this work. Conversion factors to SI units are: energy, $1 E_h = 4.3597482 \times 10^{-18}$ J; length, $1 a_0 = 0.529177249 \times$

10^{-10} m; dipole moment, $1 e a_0 = 8.478358 \times 10^{-30}$ C m; dipole polarizability, $1 e^2 a_0^2 E_h^{-1} = 1.648778 \times 10^{-41}$ C² m² J^{−1}; first dipole hyperpolarizability, $1 e^3 a_0^3 E_h^{-2} = 3.206361 \times 10^{-53}$ C³ m³ J^{−2}; and second dipole hyperpolarizability, $1 e^4 a_0^4 E_h^{-3} = 6.235378 \times 10^{-65}$ C⁴ m⁴ J^{−3}.

4. Results and discussion

SCF values calculated with all basis sets used in this study are displayed in Table 1. In Tables 2–4 we show a detailed analysis of electron correlation effects on all independent tensor components calculated with basis set A3. In Table 5 we show basis set

Table 2

Electron correlation effects on the electric dipole moment and dipole polarizability of SO₂ calculated with basis set A3 \equiv [8s6p6d2f/7s5p4d1f]

Method	μ_z	α_{xx}	α_{yy}	α_{zz}	$\bar{\alpha}$	$\Delta\alpha$
SCF	−0.8039	31.41	18.61	20.75	23.59	11.88
MP2	−0.6024	34.59	19.95	23.61	26.05	13.20
SDQ-MP4	−0.6539	34.23	19.60	23.01	25.61	13.26
MP4	−0.5915	34.65	20.00	23.88	26.18	13.15
CCSD	−0.6723	34.13	19.52	22.73	25.46	13.29
CCSD(T)	−0.6363	34.45	19.81	23.25	25.84	13.26

Table 3

Analysis of electron correlation effects on the first hyperpolarizability of SO₂ calculated with basis set A3 ≡ [8s6p6d2f/7s5p4d1f]

Method	β_{xxz}	β_{yyz}	β_{zzz}	$\bar{\beta}$
SCF	23.3	6.4	28.3	34.9
MP2	5.0	8.9	32.6	27.9
SDQ-MP4	11.9	8.3	32.0	31.3
MP4	6.0	9.5	36.5	31.3
CCSD	15.0	7.4	28.2	30.4
CCSD(T)	12.6	8.0	29.7	30.1

effects on the correlated values. Last, in Table 6 we compare our findings to select results from the literature. All molecular property values are given in this section as $\mu_\alpha/e a_0$, $\alpha_{\alpha\beta}/e^2 a_0^2 E_h^{-1}$, $\beta_{\alpha\beta\gamma}/e^3 a_0^3 E_h^{-2}$ and $\gamma_{\alpha\beta\gamma\delta}/e^4 a_0^4 E_h^{-3}$.

4.1. SCF results

Due the systematic optimization of the d-GTF, we expect the dipole polarizability to be very reliably predicted by all basis sets. All dipole moment and polarizability values are quite close to the most accurate SCF results obtained in this study. Our largest basis set P gives $\mu_z = -0.7916$ and $\alpha_{xx} = 31.32$, $\alpha_{yy} = 18.66$ and $\alpha_{zz} = 20.80$. The smallest basis set A0 yields results in agreement of 1% or better with the larger basis sets. The invariants $\bar{\alpha}$ and $\Delta\alpha$ for P are 23.59 and 11.73. A surprisingly good agreement is also present for the first dipole hyperpolarizability. Stable values are obtained for all tensor components of $\beta_{\alpha\beta\gamma}$. A0 gives a mean value $\bar{\beta} = 34.4$, only 1.7% lower than the accurate P result of 35.0. All other basis sets are significantly closer to P for this property. A0 contains only two d-GTF, a minimal composition for basis sets employed in po-

larizability calculations. Thus the fair agreement between the A0 and P second hyperpolarizability values is quite satisfactory. A0 gives for the mean $\bar{\gamma} = 1842$, which is only 10.6% lower than the most accurate 2061 obtained with basis P. All other basis sets A1–A6 and K are less than 2% from this value. We have also included in Table 1 our previous SCF calculation [11]. The total effort results in a convincingly stable SCF picture. Using a carefully optimized basis set as starting point, we have produced a sequence A1–A6 that converges to the near-Hartree–Fock results obtained with basis P. Moreover, another very large basis set, in-between A6 and P but built upon a different substrate than either, is also very close to P. This supports our claim that there is no systematic error present in our SCF values.

4.2. Electron correlation effects

Let us consider first the A3 results in Tables 2–4.

Electron correlation has a strong effect on the dipole moment of SO₂. The CCSD(T) value is -0.6363 , which represents a reduction of 20.8% of the magnitude of the SCF value. The effect on the Cartesian components of the dipole polarizability is uniform. The CCSD(T) values of $\bar{\alpha} = 25.84$ and $\Delta\alpha = 13.26$ are 9.5 and 11.6% higher than the SCF results. We observe that all post-Hartree–Fock results in Table 2 yield values reasonably close to the presumably most accurate CCSD(T).

A different picture emerges from Table 3. Although the mean $\bar{\beta}$ results obtained with SDQ-MP4, MP4, CCSD and CCSD(T) are quite close, the individual Cartesian components show significantly more important variations. The most affected is β_{xxz} . Overall, electron correlation decreases drastically this

Table 4

Analysis of electron correlation effects on the second hyperpolarizability of SO₂ calculated with basis set A3 ≡ [8s6p6d2f/7s5p4d1f]

Method	γ_{xxxx}	γ_{yyyy}	γ_{zzzz}	γ_{xxyy}	γ_{yyzz}	γ_{zzxx}	$\bar{\gamma}$
SCF	2021	1551	2640	603	665	789	2065
MP2	2884	2370	4460	979	1074	1167	3231
SDQ-MP4	3091	2224	4224	954	1018	1194	3174
MP4	3582	2538	4916	1088	1176	1352	3654
CCSD	3030	2163	3924	916	965	1154	3037
CCSD(T)	3434	2394	4364	1011	1076	1292	3390

Table 5

Basis set dependence of electron correlation effects

Basis set	Method	μ_z	$\bar{\alpha}$	$\Delta\alpha$	$\bar{\beta}$	$\bar{\gamma}$
A0	SCF	−0.7987	23.68	12.29	34.4	1846
	MP2	−0.6196	26.10	13.52	26.3	2893
	SDQ-MP4	−0.6753	25.80	13.73	32.0	2937
	MP4	−0.6168	26.29	13.52	30.9	3361
	CCSD	−0.6929	25.66	13.76	31.2	2856
	CCSD(T)	−0.6594	26.01	13.66	30.7	3195
	ECC	0.1393	2.33	0.67	−3.7	1349
A1	SCF	−0.7974	23.71	12.29	35.4	2102
	MP2	−0.6152	26.23	13.45	27.9	3342
	SDQ-MP4	−0.6702	25.90	13.64	33.4	3356
	MP4	−0.6115	26.43	13.40	32.7	3848
	CCSD	−0.6877	25.75	13.67	32.4	3234
	CCSD(T)	−0.6540	26.12	13.55	32.0	3620
	ECC	0.1434	2.41	1.26	−3.4	1518
A2	SCF	−0.8009	23.74	12.31	34.8	2116
	MP2	−0.6129	26.25	13.46	26.7	3356
	SDQ-MP4	−0.6670	25.93	13.64	32.1	3389
	MP4	−0.6072	26.45	13.40	31.3	3896
	CCSD	−0.6848	25.77	13.68	31.1	3256
	CCSD(T)	−0.6503	26.14	13.56	30.7	3635
	ECC	0.1506	2.40	1.25	−4.1	1519
A3	SCF	−0.8039	23.59	11.88	34.9	2065
	MP2	−0.6024	26.05	13.20	27.9	3231
	SDQ-MP4	−0.6539	25.61	13.26	31.3	3174
	MP4	−0.5915	26.18	13.15	31.3	3654
	CCSD	−0.6723	25.46	13.29	30.4	3037
	CCSD(T)	−0.6363	25.84	13.26	30.1	3390
	ECC	0.1676	2.25	1.38	−4.8	1325
A4	SCF	−0.8125	23.72	12.22	35.4	2108
	MP2	−0.6203	26.13	13.44	26.8	3253
	SDQ-MP4	−0.6737	25.66	13.52	31.1	3194
	MP4	−0.6111	26.22	13.36	30.5	3673
	CCSD	−0.6905	25.50	13.55	30.3	3033
	CCSD(T)	−0.6548	25.87	13.49	29.8	3386
	ECC	0.1577	2.15	1.27	−5.6	1278

component but the trend is reversed for β_{yyz} and β_{zzz} . This partial cancellation of effects is reflected on the mean value and the relative stability of the higher methods.

In marked contrast to the first hyperpolarizability, the magnitude of the components of $\gamma_{\alpha\beta\gamma\delta}$ increases with the inclusion of electron correlation. The effect is quite strong. The axial components at the CCSD(T) level of theory are $\gamma_{xxxx} = 3434$, $\gamma_{yyyy} = 2394$ and $\gamma_{zzzz} = 4364$. These values are 69.9, 54.4 and 65.3%, respectively, above the SCF results. The mean $\bar{\gamma} =$

3390 is 64.2% above the SCF value of 2065. The MP2 method yields a very reasonable description of $\gamma_{\alpha\beta\gamma\delta}$. One should also notice the systematic trend $MP4 > CCSD(T)$, although the SDQ-MP4 and CCSD results are remarkably close.

In Table 5 we collect our findings on the basis set dependence of electron correlation effects. The ECC results in this table show, convincingly enough, that even if a particular method predicts reasonable values for a molecular property, it is not obvious that a sufficiently accurate estimate of the magnitude of

Table 6

Comparison of theoretical and experimental results for the electric properties of SO₂

Method	μ_z	$\bar{\alpha}$	$\Delta\alpha$	$\bar{\beta}$	$\bar{\gamma}$
<i>Theory:</i>					
DFT ^a		24.59	13.02		
CCSDLR ^b		26.06	13.94		
DFT ^c		25.69	12.80		
DFT ^d	−0.6413	25.52	12.65		
SCF ^e	−0.7877	23.57	11.69	32.9	2038
SCF ^f	−0.7916	23.59	11.73	35.0	2061
SCF ^g	−0.8039	23.59	11.88	34.9	2065
CCSD(T) ^g	−0.6363	25.84	13.26	30.1	3390
<i>Experiment</i>					
	−0.64000 ^h	25.61 ⁱ	14.20 ^j	16 ± 47 ^k	481 ± 802 ^k
		25.452 ^l	13.75 ^k		

^a Van Gisbergen et al. [26].^b Dalskov and Sauer [27].^c Van Caillie and Amos [28].^d Cohen and Tantirungrotechai [29].^e Maroulis [11].^f Present investigation, basis set P4.^g Present investigation, basis set A3.^h Patel et al. [30].ⁱ Kumar and Meath [31].^j Murphy [32], dynamic value at 514.5 nm.^k Gentle et al. [10], measurements at 632.8 nm.^l Feng et al. [33].

electron correlation effects has been obtained. For the dipole moment we obtain ECC values of 0.1393 (A0), 0.1434 (A1), 0.1506 (A2), 0.1676 (A3) and 0.1577 (A4). Small variations are observed for the mean dipole polarizability as well. It is worth noticing that the magnitude of ECC for $\bar{\alpha}$ decreases with increasing basis set size for A1 → A4. $\Delta\alpha$ is a property more sensitive to basis set effects. The A0 value of $\Delta\alpha = 13.66$ is only 3.0% above the more accurate A3 result but the ECC doubles from A0 to A3. The mean first dipole hyperpolarizability calculated with A0 is $\bar{\beta} = 30.7$, remarkably close to the values obtained with the higher members of the basis set sequence. The ECC increases monotonically in magnitude with basis set size from A1 to A4. For the second dipole hyperpolarizability we observe more significant variations. For A0 we obtain $\bar{\gamma} = 3195$. A0 contains a minimal number of d-GTF and no f-GTF. One expects the presence of more polarization functions to increase the value of $\bar{\gamma}$. A1 and A2 give 3620 and 3635, respectively, ~ 13% above the A0 result. Further addition of polarization functions

lowers $\bar{\gamma}$ to 3390 (A3) and 3386 (A4). These values suggest a ECC estimate of 13×10^2 for $\bar{\gamma}$. The A0 ECC is close to this estimate, but is clear that the effect is overestimated by A1 and A2.

A last observation about the results of Table 5 concerns the relative performance of the higher-order methods in the calculation of the hyperpolarizability. The mean first dipole hyperpolarizability values predicted by CCSD and CCSD(T) are consistently close for all members of the sequence A0–A4. This is not the case for the second hyperpolarizability, where CCSD(T) values are systematically larger. Also, for all basis sets A0–A4 $\bar{\gamma}(\text{MP4}) > \bar{\gamma}(\text{CCSD(T)})$.

In Table 6 we compare our findings with previous theoretical and experimental results. The new theoretical dipole polarizability values have been obtained with density functional theory (DFT) methods. These are the values of Van Gisbergen et al. [26], van Caillie and Amos [28] and Cohen and Tantirungrotechai [29]. We list also the CCSDLR (couple cluster singles and doubles linear response) values of Dalskov and Sauer [27]. There is a fair agreement of

present and previous results. Our A3 CCSD(T) value for the dipole moment is -0.6363 , 0.6% lower in magnitude than the experimental equilibrium geometry result of Patel et al. [30]. It is worth noticing that the experimental value for the ground vibrational state is $\mu_{000} = -0.6425$, or barely 0.4% higher in magnitude than the equilibrium value [30]. One would normally expect the effect to amount only a few percent the most for the dipole polarizability and hyperpolarizability. Consequently, our dipole polarizability values appear to be convincingly close to the estimates of static $\bar{\alpha}$ and the dynamic $\Delta\alpha$ values in Table 6. The discrepancy between theory and experiment is obvious when we compare our hyperpolarizability values to the Kerr effect (632.8 nm) estimates reported by Gentle et al. [10]. This divergence has somehow been anticipated and explained by these authors in the careful analysis of their results.

5. Conclusions

We have obtained accurate values for the dipole moment, polarizability and hyperpolarizability of SO_2 . A very large $\text{P} \equiv [19\text{s}14\text{p}6\text{d}3\text{f}/15\text{s}10\text{p}5\text{d}2\text{f}]$ basis set is thought to provide reliable estimates of the Hartree–Fock limit for all properties: $\mu_z = -0.7916 e a_0$, $\bar{\alpha} = 23.59$ and $\Delta\alpha = 11.73 e^2 a_0^2 E_h^{-1}$, $\bar{\beta} = 35.0 e^3 a_0^3 E_h^{-2}$ and $\bar{\gamma} = 2061 e^4 a_0^4 E_h^{-3}$. Our best estimates for the electron correlation correction to the SCF polarizabilities and hyperpolarizabilities have been obtained at the CCSD(T) level of theory with a $\text{A3} \equiv [8\text{s}6\text{p}6\text{d}2\text{f}/7\text{s}5\text{p}4\text{d}1\text{f}]$ basis set, rich in d-GTF on both sulphur and oxygen. Our final prediction for the hyperpolarizability is $\bar{\beta} = 35.0 \pm 0.9 e^3 a_0^3 E_h^{-2}$ and $\bar{\gamma} = (3.4 \pm 0.2) \times 10^2 e^4 a_0^4 E_h^{-3}$.

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