Theor Chem Acc (2004) 112: 135–140
DOI 10.1007/s00214-004-0574-3

Theoretical
Chemistry Accounts

Regular article

Can STO basis sets do a good job in evaluating molecular electromagnetic properties? II: Second hyperpolarizability of H_2O, CH_4 and NH_3 according to the TDHF theory

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Received: 15 July 2003 / Accepted: 20 January 2004 /

Abstract. The assessment of the performance of STO basis sets for the ab initio estimation of nonlinear electromagnetic response properties of molecules, using a Time Dependent Hartree-Fock procedure, has been extended from the first to the second dynamic hyperpolarizability of three bench polyatomics (H_2O, CH_4, NH_3). Calculations based on extended basis sets are reported and briefly discussed in order to provide a wider perspective on the existing comparisons.

Keywords: NLO molecular properties – Hyperpolarizability – TDHF theory – STO basis set calculations

Introduction

The identification and screening of potentially interesting molecular candidates for nonlinear optics (NLO) and photonic applications can take advantage of cross-disciplinary experience gained from various research fields, not least quantum chemistry. The topic of the response of materials to intense electromagnetic (e.m.) radiation is indisputably a very complex one, particularly in the case of condensed phase systems. Any microscopic description of the electric polarization observed in this case should take into account optical susceptibilities, which are in turn built up from nonlocal correlation functions [1]. Diluted-gas phase experiments put quantum chemistry in more favorable position, because the absence of appreciable intermolecular effects enables important simplifications to be made to the formalism due to the essentially insignificant difference between external and local e.m. polarizing fields. Under such conditions, in fact, the optical nonlinear susceptibilities of the various orders can more simply be replaced by the proper hyperpolarizabilities of the isolated, active molecules [1, 2, 3, 4].

This aside, the estimation of these molecular properties poses severe problems to the computational quantum chemist. Obtaining accurate ab initio hyperpolarizability estimates, even for small-size molecules, is generally recognized to be a challenging task, considering the many features that must be taken into account (including basis set selection, electron-correlation appraisal, vibrational corrections, and dispersion effects [5, 6]).

In a previous paper from this journal [7] (hereafter referred to as I), we reported results for the first electric-dipole hyperpolarizability tensor β of a few simple polyatomics (H_2O, CH_4, NH_3). In view of the level of theory utilized (TDHF approximation [8, 9, 10, 11, 12]), we are permitted to regard these values as reasonable estimates for the property investigated at most, considering for instance that we neglected the (very important) role played by electron correlation effects. The peculiarity endowing our β results with some significance derives essentially from the basis set choice; in our case a many-center STO truncated expansion, a little unusual in today's computational quantum chemistry, traditionally dominated by GTO implementations. The present work is the natural complement to I (to which we refer for additional details). The data reported concern the second electric-dipole hyperpolarizability tensor γ of the same molecules considered in I, with the adoption of the same level of theory (TDHF approximation) and in terms of the same STO basis sets employed for the first hyperpolarizability β predictions.

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The layout of the paper is as follows. After a brief presentation of the formalism involved (Sect. 2), the results obtained for the second hyperpolarizability of H_2O, CH_4 and NH_3 are presented and discussed in Sect. 3, along lines running parallel to those followed in I.

TDHF formalism and its implementation: a brief review

Thanks to much theoretical work, appropriate algorithms for the evaluation of molecular e.m. response functions, at various levels of sophistication, are currently available. In particular, explicit formulae for the dynamic dipole polarizability and the first two hyperpolarizabilities have been brought to the attention of potential users [5, 6, 8, 9, 10, 11, 12, 15, 16, 17, 18, 19]. Even though there aren't any strong motivations for revisiting questions concerning the formalism, a short discussion of some of its basic tenets, stressing features of our TDHF treatments, will be useful.

Although general, open-ended approaches to hyperpolarizabilities of arbitrary order have been set up [5], in its present version our computer package does not allow us to evaluate the e.m. response of molecular systems beyond the second hyperpolarizability. A first feature characterizing our implemented algorithm is that the field-modified MOs are perturbatively expanded in terms of the canonical MOs generated by the preliminary solution of the unperturbed SCF problem, so that a four-index transformation from the original STO atomic basis set is a mandatory step of our procedure. This is, admittedly, a rather standard way of proceeding, widely implemented over many years. Newer approaches (like the so-called "direct" and "semidirect" methods [20, 21]) for the evaluation of observables (in particular, hyperpolarizabilities) have been suggested and applied, but will not be commented on further.

Assuming that the light-matter interaction is adequately described with the electric-dipole approximation (length gauge [10]), and ignoring the role of rotovibrational motions, in the spirit of the Born-Oppenheimer approximation our TDHF formulation assumes in full generality that the electrons are subjected to the simultaneous action of several, independent, oscillating, polar electric fields, so that the single polar perturbed MOs can be expressed according to the following compact expansion involving tensor (dyadics) of increasing rank [22]:

$$
\begin{aligned}
\phi_j(t) = \phi_j^{(0)} &+ \sum_A \vec{E}^{\mathrm{A}}\left(\omega^{\mathrm{A}}\right)\cdot\vec{\phi}_j^{\mathrm{A}}\left(t;\omega^{\mathrm{A}}\right) \\
&+ \sum_{\mathrm{AB}} \vec{E}^{\mathrm{A}}\left(\omega^{\mathrm{A}}\right)\vec{E}^{\mathrm{B}}\left(\omega^{\mathrm{B}}\right) : \overset{\leftrightarrow}{\phi}_j^{\mathrm{AB}}\left(t;\omega^{\mathrm{A}},\omega^{\mathrm{B}}\right) \\
&+ \sum_{\mathrm{ABC}} \vec{E}^{\mathrm{A}}\left(\omega^{\mathrm{A}}\right)\vec{E}^{\mathrm{B}}\left(\omega^{\mathrm{B}}\right)\vec{E}^{\mathrm{C}}\left(\omega^{\mathrm{C}}\right) \vdots \overset{\leftrightarrow}{\phi}_j^{\mathrm{ABC}} \\
&\times \left(t;\omega^{\mathrm{A}},\omega^{\mathrm{B}},\omega^{\mathrm{C}}\right) + \ldots
\end{aligned}
\tag{1}
$$

The superscripts A, B, and C identify the various independent electric fields $\vec{E}$ applied to the molecule, each characterized by a given frequency and (linear) polarization.

For closed-shell molecules, the field-induced contributions to the electric dipole moment $\vec{\mu}(t) = 2\sum_{j=1}^{\mathrm{occ}}\left\langle \phi_j(t)\middle|\vec{\mu}_{\mathrm{op}}\middle|\phi_j(t)\right\rangle$ follow in a straightforward way from Eq. 1. In particular, the second electric dipole hyperpolarizability is easily extracted from the expansion, with the result (atomic units are used throughout this paper):

$$
\begin{aligned}
\gamma_{\lambda\mu\nu\rho}(\omega,\omega',\omega'') = {}& -12\sum_{j}^{\mathrm{occ}}\sum_{a}^{\mathrm{unocc}} P_{aj}^{\lambda}\left[U_{aj}^{\mu\nu\rho}(\omega,\omega',\omega'') + U_{aj}^{\mu\nu\rho}(-\omega,-\omega',-\omega'')\right] \\
& + 4\sum_{ij}^{\mathrm{occ}}\sum_{a}^{\mathrm{unocc}} P_{ij}^{\lambda}[U_{aj}^{\mu}(\omega)U_{aj}^{\nu\rho}(-\omega',\omega'') + U_{ai}^{\nu}(\omega')U_{aj}^{\mu\rho}(-\omega',-\omega'') + U_{ai}^{\rho}(\omega'')U_{aj}^{\mu\nu}(-\omega,-\omega') \\
& \qquad + U_{aj}^{\mu}(\omega)U_{ai}^{\nu\rho}(\omega',\omega'') + U_{aj}^{\nu}(-\omega')U_{ai}^{\mu\rho}(\omega,\omega'') + U_{aj}^{\rho}(-\omega'')U_{ai}^{\mu\nu}(\omega,\omega')] \\
& - 4\sum_{ij}^{\mathrm{occ}}\sum_{a}^{\mathrm{unocc}} P_{aj}^{\lambda}[U_{ai}^{\mu}(\omega)U_{ji}^{\nu\rho}(-\omega',-\omega'') + U_{ai}^{\nu}(\omega')U_{ji}^{\mu\rho}(-\omega,-\omega'') + U_{ai}^{\rho}(\omega'')U_{ji}^{\mu\nu}(-\omega,-\omega') \\
& \qquad + U_{ai}^{\mu}(-\omega)U_{ji}^{\nu\rho}(\omega',\omega'') + U_{ai}^{\nu}(-\omega')U_{ji}^{\mu\rho}(\omega,\omega'') + U_{ai}^{\rho}(-\omega'')U_{ji}^{\mu\nu}(\omega,\omega')] \\
& - 4\sum_{i}^{\mathrm{occ}}\sum_{ab}^{\mathrm{unocc}} P_{ab}^{\lambda}[U_{ai}^{\mu}(\omega)U_{bi}^{\nu\rho}(-\omega',-\omega'') + U_{ai}^{\nu}(\omega')U_{bi}^{\mu\rho}(-\omega,-\omega'') + U_{ai}^{\rho}(\omega'')U_{bi}^{\mu\nu}(-\omega,-\omega') \\
& \qquad + U_{ai}^{\mu}(-\omega)U_{bi}^{\nu\rho}(\omega',\omega'') + U_{ai}^{\nu}(-\omega')U_{bi}^{\mu\rho}(\omega,\omega'') + U_{ai}^{\rho}(-\omega'')U_{bi}^{\mu\nu}(\omega,\omega')]
\end{aligned}
\tag{2}
$$

where $\vec{U}_{rs}(\omega)$, $\overset{\leftrightarrow}{U}_{rs}(\omega, \omega')$, and $\overset{\leftrightarrow}{U}_{rs}(\omega, \omega', \omega'')$ are transition tensors of rank one, two and three, respectively, each relative to a definite pair (*r*,*s*) of canonical SCF MOs. Explicit formulae for the expansion of the tensor quantities $\vec{\phi}_j^{\mathrm{A}}\left(t; \omega^{\mathrm{A}}\right)$ and $\overset{\leftrightarrow}{\phi}_j^{\mathrm{AB}}\left(t; \omega^{\mathrm{A}}, \omega^{\mathrm{B}}\right)$ can be found in I. Here we exclusively report the analogous expansion of the third-rank tensor $\overset{\leftrightarrow}{\phi}_j^{\mathrm{ABC}}\left(t; \omega^{\mathrm{A}}, \omega^{\mathrm{B}}, \omega^{\mathrm{C}}\right)$, which is inescapably required for a correct evaluation of the Cartesian components of the electric dipole second hyperpolarizability γ, Eq. 2.

$$
\begin{aligned}
\phi_j^{\mathrm{ABC}}\left(t; \omega^{\mathrm{A}}, \omega^{\mathrm{B}}, \omega^{\mathrm{C}}\right) = \tfrac{1}{8} \sum_r \phi_r^{(0)} [& e^{i\left(\omega^{\mathrm{A}} + \omega^{\mathrm{B}} + \omega^{\mathrm{C}}\right)t} U_{rj}^{\mathrm{ABC}}\left(\omega^{\mathrm{A}}, \omega^{\mathrm{B}}, \omega^{\mathrm{C}}\right) \\
& + e^{-i\left(\omega^{\mathrm{A}} + \omega^{\mathrm{B}} + \omega^{\mathrm{C}}\right)t} U_{rj}^{\mathrm{ABC}}\left(-\omega^{\mathrm{A}}, -\omega^{\mathrm{B}}, -\omega^{\mathrm{C}}\right) \\
& + e^{i\left(\omega^{\mathrm{A}} + \omega^{\mathrm{B}} - \omega^{\mathrm{C}}\right)t} U_{rj}^{\mathrm{ABC}}\left(\omega^{\mathrm{A}}, \omega^{\mathrm{B}}, -\omega^{\mathrm{C}}\right) \\
& + e^{-i\left(\omega^{\mathrm{A}} + \omega^{\mathrm{B}} - \omega^{\mathrm{C}}\right)t} U_{rj}^{\mathrm{ABC}}\left(-\omega^{\mathrm{A}}, -\omega^{\mathrm{B}}, \omega^{\mathrm{C}}\right) \\
& + e^{i\left(\omega^{\mathrm{A}} - \omega^{\mathrm{B}} + \omega^{\mathrm{C}}\right)t} U_{rj}^{\mathrm{ABC}}\left(\omega^{\mathrm{A}}, -\omega^{\mathrm{B}}, \omega^{\mathrm{C}}\right) \\
& + e^{-i\left(\omega^{\mathrm{A}} - \omega^{\mathrm{B}} + \omega^{\mathrm{C}}\right)t} U_{rj}^{\mathrm{ABC}}\left(-\omega^{\mathrm{A}}, \omega^{\mathrm{B}}, -\omega^{\mathrm{C}}\right) \\
& + e^{i\left(-\omega^{\mathrm{A}} + \omega^{\mathrm{B}} + \omega^{\mathrm{C}}\right)t} U_{rj}^{\mathrm{ABC}}\left(-\omega^{\mathrm{A}}, \omega^{\mathrm{B}}, \omega^{\mathrm{C}}\right) \\
& + e^{-i\left(-\omega^{\mathrm{A}} + \omega^{\mathrm{B}} + \omega^{\mathrm{C}}\right)t} U_{rj}^{\mathrm{ABC}}\left(\omega^{\mathrm{A}}, -\omega^{\mathrm{B}}, -\omega^{\mathrm{C}}\right)
\end{aligned}
\tag{3}
$$

$P_{rs}^{\lambda} \equiv -\langle \phi_r^{(0)} | r_\lambda | \phi_s^{(0)} \rangle$ is the (*r*,*s*) matrix element, in the unperturbed canonical MO basis set, of the λ^{th} component of the electric dipole moment operator, $\vec{\mu}_{\mathrm{op}} = -\vec{r}$. It should be observed that, contrary to the cases of both linear response and first hyperpolarizability β, the evaluation of the second hyperpolarizability γ cannot get rid of transition tensors $\overset{\leftrightarrow}{U}^{\mathrm{AB}}$ involving pairs (*r*,*s*) of simultaneously occupied canonical MOs.

A glossary of the main NLO processes that allow us to extract information about hyperpolarizabilities can be found elsewhere [14, 15, 16, 23]. Limiting ourselves to the cubic response, we cite: a) third harmonic generation (THG), $\omega \rightarrow 3\omega$; in other words the frequency triplication effect caused by an incident laser beam of frequency $\omega[\gamma(-3\omega; \omega, \omega, \omega)$ is the usual notation for the corresponding hyperpolarizability]; b) static electric field induced second harmonic generation (ESHG; also dc SHG or EFISH), the frequency doubling effect produced from an incident laser beam in the presence of an electrostatic field [associated hyperpolarizability, $\gamma(-2\omega; \omega, \omega, 0)$]; c) degenerate three wave mixing (also nonlinear refractive index or intensity dependent refractive index IDRI), the effect observed when three distinguishable beams of frequency ω interact to generate a fourth beam with the same frequency $[\gamma(-\omega; \omega, \omega, -\omega)]$; d) coherent anti-Stokes Raman scattering (CARS), the effect arising from the coupling of a strong laser beam (frequency ω) to a weaker beam (frequency ω') to generate a beam of frequency $2\omega - \omega'[\gamma(-2\omega + \omega'; \omega, \omega, -\omega')]$. The static cubic response obviously corresponds to $\omega = \omega' = \omega'' = 0$.

Expressions for the TDHF equations relative to the tensor amplitudes $\vec{U}^{\mathrm{A}}, \overset{\leftrightarrow}{U}^{\mathrm{AB}}, \overset{\leftrightarrow}{U}^{\mathrm{ABC}}$ that appear in Eq. 2 can be derived at the cost of noticeable labor. As far as the present work is concerned, we emphasize that, according to our formulation, the evaluation of the nonlinear e.m. response parameters is approached in full generality, avoiding its reduction to a set of answers for particular effects such as those listed above. The resolvent equations for $\vec{U}^{\mathrm{A}}$ and $\overset{\leftrightarrow}{U}^{\mathrm{AB}}$ have already been put forward in I. The equations for $\overset{\leftrightarrow}{U}^{\mathrm{ABC}}$ are structurally similar to those reported in I and will not be quoted. For further information on this issue, we refer the reader to that paper.

Results

Static hyperpolarizability

As already pointed out, the hyperpolarizability calculations reported refer exclusively to the electronic contribution to the response function (Born-Oppenheimer approximation, at the experimental equilibrium geometry). We will maintain a close correspondence with our findings from the previous paper I [7] concerning dipole polarizability and first hyperpolarizability.

Static property data for the three molecules investigated are collected in the Tables 1, 2, and 3, for H_2O, CH_4 and NH_3, respectively. For each molecular system, we report several estimated values relative to independent components of the second dipole hyperpolarizability tensor γ, as obtained from different STO basis sets. In addition to these independent components, the scalar component of the tensor, in other words its isotropic average $\bar{\gamma} = \left(\frac{1}{15}\right)\sum_{\xi\eta}\left[\gamma_{\xi\xi\eta\eta} + \gamma_{\xi\eta\eta\xi} + \gamma_{\xi\eta\xi\eta}\right](\xi, \eta \equiv x, y, z)$, is also included. (As an alternative notation, $\bar{\gamma} = \langle\gamma\rangle_{zzzz}$, where $\langle\rangle$ denotes the isotropic average and z is the space-fixed direction defined by the applied field [15]).

Comments concerning the basis sets employed and their construction have already been made in paper I [7]. They keep their full validity in the present context, where the γ data reported refer to exactly the same basis sets as labeled in I, to allow us to establish an immediate connection with both polarizability and first hyperpolarizability behavior.

As appropriately remarked elsewhere [5], the fact that the prediction of dipole hyperpolarizabilities, in the length gauge, involves products of matrix elements of the electron position operator, demands an adequate description of the electronic charge distribution in the more diffuse molecular regions. Proper basis prescriptions for estimating dipole moments require generalizations (usually basis extensions) to achieve significant results, even at the level of dipole polarizability α, and still further extensions for the prediction of successive hyperpolarizabilities β and γ. But there are consequences, in the sense that all contributions to α have the same sign, so that the larger the basis set employed, generally the better the estimated polarizability, and this is usually true of γ as well, while β seems to suffer from a more marked inherent instability. The γ data reported in the Tables 1, 2, and 3 offer a good example of the behavior schematically described above, in clear conflict with that exhibited by the first dipole hyperpolarizability β (see Tables 1, 2, 3 of I). The basis sets elaborated are essentially built up starting from a "core" basis set through a "decoration" procedure consisting of progressive addition of properly chosen polarization STOs [7], up to reaching a maximum extension (83 STOs for H_2O, 77 STOs for CH_4, 83 STOs for NH_3), principally dictated by reasons of plausibly reached saturation. Huge changes in the predicted property are immediately perceived as we run through the several calculations, the magnitude of the jump between the first and the last test reported being particularly large in the cases of H_2O and CH_4. A rationale of the less conformal behavior of NH_3 can be inferred considering the basis set construction adopted for this molecule and discussed in I.

Table 1. Independent components of the static second dipole hyperpolarizability of the H_2O molecule (in a.u.). The molecule (equilibrium geometry) lies in the (xz)-plane, with z-axis along the electric dipole

Parameter	DPA	B1	B2	B3	B4	B5	B6	B7	MA (from [24])	SB (from [5])	AI (from [25])	KSAY (from [17])
γ_{xxxx}	50.11	235.69	238.77	240.82	395.32	408.56	551.93	562.85	569	550	473.4	572.73
γ_{yyyy}	18.38	338.68	342.77	344.68	1258.61	1306.62	1428.62	1436.81	1422	1500	1225	1413.8
γ_{zzzz}	39.87	267.43	269.34	270.49	730.30	745.62	918.81	922.90	907	920	764.5	888.17
γ_{xxyy}	8.32	82.31	83.13	83.58	292.06	291.99	345.04	347.20	338	350	293.9	340.32
γ_{yyzz}	8.20	92.66	93.54	93.98	334.50	339.36	389.72	391.53	389	400	325.5	385.12
γ_{zzxx}	54.51	136.49	138.02	139.14	240.52	249.39	286.62	291.53	287	280	282.0	284.01
$\bar{\gamma}$	50.08	292.94	296.05	297.88	823.68	844.46	988.42	996.62	985	1006	853.1	978.72

Table 2. Independent components of the static second dipole hyperpolarizability of the CH_4 molecule (in a.u.). Molecule in its equilibrium geometry

Parameter	B1	B2	B3	B4	B5	B6	B7	MA (from [26])	SB (from [9])	BS (from [27])	HJ (from [28])
γ_{xxxx}	16.644	38.005	156.35	201.44	270.51	1259.52	1473.72	1806	299.111	-	-
γ_{xxyy}	5.267	15.169	42.407	54.06	74.44	518.10	566.37	667	227.045	-	-
$\bar{\gamma}$	16.307	41.006	144.70	185.74	251.63	1377.43	1563.88	1884	451.921	1882	1870.5

Table 3. Independent components of the static second dipole hyperpolarizability of the NH_3 molecule (in a.u.). The molecule is considered at its equilibrium geometry, with the z-axis along the dipole moment and pointing toward the N atom

Parameter	B1	B2	B3	B4	B5	B6	B7	MA (from [29])	SB (from [5])	KSAY (from [17])	AI (from [25])
γ_{xxxx}	1151.53	1174.67	1170.23	1199.28	1161.55	1218.32	1214.58	1280	1200	1317.7	1089
γ_{xxxz}	−143.23	−115.95	−123.47	−127.10	−129.09	−108.91	−105.57	−67	-	−73.171	-
γ_{xxzz}	917.26	935.77	920.42	1097.85	1120.82	1122.92	1117.90	1143	1100	1106.3	1082
γ_{zzzz}	2439.91	2469.31	3294.40	4301.79	4534.88	4602.13	4608.10	4531	4500	4576.7	4300
$\bar{\gamma}$	1835.94	1868.97	2019.34	2378.25	2423.13	2468.53	2463.72	2503	2420	2503.15	2306

In particular, the very delicate nature of nonlinear response properties is clearly exhibited. Our results for H_2O compare very well with existing estimates from different sources, with NH_3 placed rather close to H_2O in this respect, while CH_4 displays a worse agreement, an effect reasonably ascribable to imperfect "decoration" of the "core" basis set by polarization STOs.

Hyperpolarizability and frequency dependence

Dynamic hyperpolarizability data for H_2O, CH_4 and NH_3 are collected in Table 4, Table 5 and Table 6, respectively. The exploration of the dispersion effects at $\lambda = 694.3$ nm ($\omega = 0.0656$ a.u.) corresponds to a now standard practice in computational studies of hyperpolarizabilities.

Table 4. Second dipole hyperpolarizability of the H_2O molecule (in a.u.) at $\lambda = 694.3$ nm

THG			ESHG				IDRI			EOKE and dc OR			
$\gamma(-3\omega;\omega,\omega,\omega)$	B7	SB (from [5])	$\gamma(-2\omega;\omega,\omega,0)$	B7	KSAY (from [17])	SB (from [5])	$\gamma(-\omega;\omega,\omega,-\omega)$	B7	SB (from [5])	$\gamma(-\omega;\omega,0,0)$	B7	AI (from [25])	SB (from [5])
xxxx	744.88		xxxx	645.16	654.79		xxxx	615.89		xxxx	588.27	492.6	
xxyy	491.96		xxyy	414.32	404.97		xxyy	401.67		xxyy	365.39	306.7	
xxzz	398.25		xxzz	339.74	330.37		xxzz	325.98		xxzz	305.58	294.0	
yyxx	646.80		xyyx	416.01	405.93		yyxx	401.66		yyxx	383.40	328.0	
yyyy	2381.15		xzzx	341.97	331.72		yyyy	1669.80		yyyy	1546.3	1306.	
yyzz	689.95		yxxy	439.93	428.65		yyzz	450.77		yyzz	428.19	356.7	
zzxx	431.89		yyxx	462.12	450.31		zzxx	325.95		zzxx	310.49	299.1	
zzyy	568.16		yyyy	1811.49	1771.2		zzyy	450.83		zzyy	414.81	341.5	
zzzz	1320.01		yyzz	509.08	497.92		zzzz	1032.28		zzzz	974.88	806.1	
$\overline{\gamma}^{(a)}$	1534.61	1515.0	yzzy	487.02	475.69		$\overline{\gamma}^{(a)}$	1134.97	1139.0	$\overline{\gamma}^{(a)}$	1063.5	906.2	1069
			zxxz	348.04	337.39								
			zzxx	351.85	341.66								
			zyyz	468.94	458.78								
			zzyy	472.72	463.67								
			zzzz	1095.07	1052.2								
			$\overline{\gamma}'^{(b)}$	1217.11	1190.0	1216.0							

[a] See text; [b] $\overline{\gamma}' = \frac{1}{5}\sum_{ij}\left(2\gamma_{iijj} + \gamma_{ijji}\right)$

Table 5. Second dipole hyperpolarizability of the CH_4 molecule (in a.u.) at $\lambda = 694.3$ nm

THG			ESHG			IDRI			EOKE and dc OR		
$\gamma(-3\omega;\omega,\omega,\omega)$	B7	SB (from [9])	$\gamma(-2\omega;\omega,\omega,0)$	B7	SB (from [9])	$\gamma(-\omega;\omega,\omega,-\omega)$	B7	SB (from [9])	$\gamma(-\omega;\omega,0,0)$	B7	SB (from [9])
xxxx	2045.20	−4.002	xxxx	1727.48	−7.919	xxxx	1635.43	−9.956	xxxx	1550.81	−10.127
xxzz	794.71	85.151	xxzz	667.98	74.406	xxzz	630.89	71.849	xxzz	596.72	69.044
$\overline{\gamma}$	2180.77	99.78	$\overline{\gamma}$	1838.06	84.535	$\overline{\gamma}$	1738.31	80.245	$\overline{\gamma}$	1646.55	76.777

Table 6. Second dipole hyperpolarizability of the NH_3 molecule (in a.u.) at $\lambda = 694.3$ nm

THG			ESHG				IDRI			EOKE and dc OR			
$\gamma(-3\omega;\omega,\omega,\omega)$	B7	SB (from [5])	$\gamma(-2\omega;\omega,\omega,0)$	B7	KSAY (from [17])	SB (from [5])	$\gamma(-\omega;\omega,\omega,-\omega)$	B7	SB (from [5])	$\gamma(-\omega;\omega,0,0)$	B7	AI (from [25])	SB (from [5])
xxxx	1899.39		xxxx	1500.12	1618.3		xxxx	1395.49		xxxx	1298.55	1150.	
xxyy	633.13		xxyy	493.51	534.88		xxyy	465.10		xxyy	429.54	380.6	
xxzz	2011.56		xxzz	1483.65	1466.4		xxzz	1417.09		xxzz	1209.06	1154	
zzxx	3258.32		yxxy	513.10	548.51		zzxx	1415.63		zzxx	1301.91	1261	
zzzz	11106.11		zzxx	1766.40	1730.0		zzzz	5876.18		zzzz	5181.21	4771	
$\overline{\gamma}$	5342.18	4925	zxxz	1673.89	1637.7		$\overline{\gamma}$	3052.56	2937.0	$\overline{\gamma}$	2731.87	2533	2652
			xzzx	1529.62	1503.9								
			xxxz	-144.09	-104.41								
			xxzx	-147.60	-108.45								
			zxxx	-158.21	-121.01								
			zzzz	6737.68	6616.6								
			$\overline{\gamma}$	3445.0	3457.7	3276.0							

A simple glance at the contents of Tables 4, 5, and 6 shows that only estimates from a single basis set have been reported, corresponding to the largest one elaborated by us in each case. The entries collected in the tables refer to specific NLO processes involving the second hyperpolarizability (see Sect. 2). Despite the rather reduced range of available comparisons, the conclusions stemming from the inspection of the tables correlate well to those drawn from the analysis of the static data, and confirm further remarks reported in I, on the basis of the first hyperpolarizability behavior.

The extension to the second hyperpolarizability of the study of the role of STOs in TDHF calculations of NLO properties of simple molecules does not change appreciably what had emerged from I. Although a considerable reduction of the basis extension typically required by GTO calculations can be recognized, the general feeling of the present authors is still one of substantial dissatisfaction. The "basis set representability disease" referred to in I, so marked in the case of hyperpolarizability predictions, will probably continue to constitute a nightmare in computational quantum chemistry.

Acknowledgements. This research has been partially supported by funds provided by the Italian Consiglio Nazionale delle Ricerche (contribution n. CTB 00.00650.PF34) and Pisa University (fondi di Ateneo, ex 60%, years 2001–2002).

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