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

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Abstract. The performance of STO basis sets for the ab initio estimation of the nonlinear electromagnetic response properties of molecules, in terms of a time-dependent Hartree–Fock procedure, is investigated. Applications to the case of the first dynamic hyperpolarizability of three simple polyatomics (H_2O, CH_4, NH_3) adopting several extended basis sets are reported and discussed. Independent estimates for the observables investigated obtained by the same approach in terms of Gaussian basis sets are confronted with our findings in the search for recipes of possible utility.

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

Introduction

There is general consensus that by virtue of their highly interdisciplinary nature, modern materials sciences can take great advantage of effective coordination of experiences matured in such different research areas as condensed matter and statistical physics, and quantum and computational chemistry, before synthetic chemists get involved. This is particularly true in the field of nonlinear optics (NLO) and photonics, where the ambitious program of "designing" materials of potential significance for manufacturing innovative devices (communication/information storage and processing, signal switching, etc.) is continuing to attract lively attention [1].

"To the theoretical chemist, NLO means the nonlinear (electromagnetic) response of a molecule to a time-dependent electric field", according to a concise statement found in the literature [2]. More specifically, quantum chemists feel themselves in the "hot" area of the field [3] and believe firmly that progress in NLO cannot occur without recourse to the development and the implementation of computational procedures rooted in modern molecular electronic structure methodologies. Understanding what determines the onset of the electromagnetic (e.m.) response and the role of specific functional groups in a molecule provides, in their view, an essential screening instrument for selecting potentially interesting molecular candidates [4].

The description of the response (optical polarization) of a given material subjected to the action of e.m. fields involves, in general, a complex formulation in terms of optical susceptibilities [5]. Such a formulation is uselessly complicated in the case of diluted gas-phase materials, i.e., essentially noninteracting molecules, where the average electric field acting in the medium can be assumed to be the same as the externally applied one, and the optical nonlinear susceptibilities of the various orders are simply replaced by the hierarchy of hyperpolarizabilities of a single isolated molecule [6]. Measurements of hyperpolarizabilities in the gas phase surely put theoreticians in the most favorable position for comparing their calculated estimates, because the adequacy of the (usually manifold) approximations introduced in the study of these definitely hard-to-compute properties is much better assessed.

On the theoretical side, it can be remarked that the study of the e.m. response functions of atoms and molecules has, generally speaking, exploited (and possibly incremented) the paraphernalia of quantum chemistry techniques to which is traceable the enormous progress in our understanding of the molecular electronic structure and dynamics. Allowance for electron correlation has long been known to constitute a decisive step for

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achieving chemical accuracy in energy calculations. The recognition that the electron correlation role cannot be neglected for accurate estimates of molecular hyperpolarizabilities is more recent, and stems from computational experience in terms of a host of algorithms (MP2, MP4, SDCI, CCSD are acronyms for a few of them) [2, 3, 7, 8, 9, 10, 11, 12]. According to such evidence, it has become clear that correlation effects should be appraised to a substantial degree, well beyond that characterizing simpler "mean-field" treatments like the time-dependent Hartree–Fock (TDHF) theory (or, equivalently, RPA) [7, 13, 14, 15, 16, 17], before one can speak of accurate hyperpolarizibility estimates. Considering, in addition, that vibro-rotational "corrections" are generally not ignorable and are even important [3, 10, 11, 18], it is a firm belief that theoreticians working in the field are confronted with a truly challenging problem.

The results presented in this paper concern the first hyperpolarizability of a few simple polyatomics (H_2O, CH_4, NH_3) [data for the second hyperpolarizability of the same molecules are deferred to a successive publication]. In view of the level of theory utilized (TDHF approximation) and considering the preceding remarks, the values obtained are consequently to be regarded at most as reasonable estimates for the property investigated, granted that the TDHF equations involved in the procedure have been accurately solved. On this point we think it suitable to dwell a little bit, with the intent of providing a better perspective to our calculations.

Ab initio estimates of molecular properties are known to pose reliability problems related to the effective completeness of the one-electron basis sets usually adopted for implementing the calculation procedures. This basis-set dependence, which is generally different for the various properties evaluated, can entail inaccurate predictions or even failures as the significant features of the electronic wavefunctions involved have been ill-captured as a consequence of the improper expansions used. Dynamic hyperpolarizabilities suffer to a particularly high degree from this "basis set representability disease", which must be admitted to exist regardless of the more or less approximate level of theory employed.

The TDHF approximation utilized in this paper does not make an exception. The unfortunate fact is that the recourse to truncated expansions, as an expedient to reduce the original SCF equations to a tractable, algebraic problem, can lead one to miss salient features of the correct solutions in significant regions of the electronic charge distribution (presumably the outermost ones, in the case of perturbations induced by electric fields), with possibly dramatic consequences in the prediction of sensitive observables, such as hyperpolarizabilities.

The return to the original integro-differential structure of the SCF problem, followed by the development of finite difference and finite elements techniques on an appropriate grid resulting from the parcellization of a suitable large "molecular box", suggests itself as a valuable alternative permitting one to by-pass the necessity of basis set expansions. Applications in the case of atoms and diatomics can be quoted [19, 20, 21], but to the best of our knowledge we are not aware of extensions to more complex systems. More modestly, our strategy in this paper recognizes the great advantages stemming from the recourse to truncated basis sets, with the notable novelty that we explore the role of expansions involving Slater-type orbitals (STOs), at clear variance with the almost universal adoption of Gaussian-type orbitals (GTOs) nowadays well documented.

According to a widely accepted view, STOs are in principle better suited as basis functions than GTOs, the popularity of the latter being to a large extent a consequence of the availability of accurate and efficiently organized computational codes. The basic superiority of STOs by reason of their more adequate behavior, both in proximity to and at a large distance from the nuclei, is customarily commented on in terms of the larger extension of GTO basis sets compared to the STO ones for achieving comparable predictive accuracy [22, 23]. After having been revitalized, today STOs have taken on a new lease of life, as documented by many publications to be found in the literature [24]. The present paper places itself as an addition to such a long list, on a theme of recognized interest.

A sketch of the TDHF formalism and its implementation

Much theoretical work has led to the development of appropriate algorithms for the evaluation of molecular e.m. response functions at different levels of sophistication. In particular, explicit formulae for dynamic polarizability and the first two hyperpolarizabilities are now available in the literature [2, 3, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 25, 26]. Here we shall limit ourselves to a short presentation of some basic results, stressing some peculiar features of our TDHF treatment.

Although general, open-ended approaches to hyperpolarizabilities of arbitrary order could be set up [8], in its present version our home-made computer package does not allow evaluation of the e.m. response of molecular systems beyond the second hyperpolarizability. A first significant feature of our 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 required step of our procedure. This is actually a rather standard way of proceeding, largely implemented over the years. Newer approaches (e.g., the so-called direct and semidirect methods [27, 28]) for the evaluation of observables (in particular, hyperpolarizabilities) have been suggested and applied, but will not be commented on further. The validity of the electric-dipole approximation, with complete neglect of higher electric-multipole effects, is supposed to hold, the role of vibro-rotational distortions being ignored as well. In the framework of these approximations, we have kept to a general formulation, assuming that the molecule is subjected to the simultaneous action of several oscillating electric fields, so that the single perturbed MOs can be expressed according to the following compact expansion involving tensors (dyadics) of increasing rank [29],

$$\phi_j(t) = \phi_j^{(0)} + \sum_A \overrightarrow{\varepsilon}^A\left(\omega^A\right) \cdot \vec{\phi}_j^A\left(t; \omega^A\right) + \sum_{A,B} \overrightarrow{\varepsilon}^A\left(\omega^A\right)\overrightarrow{\varepsilon}^B\left(\omega^B\right) : \vec{\phi}_j^{AB}\left(t; \omega^A, \omega^B\right) + \ldots\ldots \tag{1}$$

The superscripts A, B, ... identify the various independent fields $\overrightarrow{\varepsilon}$ acting on the molecule, each characterized by a given frequency and (linear) polarization.

The tensor quantities appearing in Eq. 1

$$\begin{aligned}\vec{\phi}_j^A(t;\omega^A) &= \frac{1}{2}\sum_r \phi_r^{(0)}\left[e^{i\omega^A t}\vec{U}_{rj}^A(\omega^A) + e^{-i\omega^A t}\vec{U}_{rj}^A(-\omega^A)\right] \\ \vec{\phi}_j^{AB}\left(t;\omega^A,\omega^B\right) &= \frac{1}{4}\sum_r \phi_r^{(0)} \cdot [e^{i\left(\omega^A+\omega^B\right)t}\vec{U}_{rj}^{AB}\left(\omega^A,\omega^B\right) \\ &\quad + e^{-i(\omega^A+\omega^B)t} \\ &\quad \vec{U}_{rj}^{AB}(-\omega^A,-\omega^B) + e^{i(\omega^A-\omega^B)t}\vec{U}_{rj}^{AB}\left(\omega^A,-\omega^B\right) \\ &\quad + e^{-i\left(\omega^A-\omega^B\right)t}\vec{U}_{rj}^{AB}\left(-\omega^A,\omega^B\right)]\end{aligned} \tag{2}$$

involve expansions in terms of the canonical unperturbed SCF MOs. The explicit presence of the coefficients 1/2, 1/4, ... ensures the same static limit for all hyperpolarizabilities of the same order [10].

For closed-shell molecules, the field-induced contribution to the electric dipole moment $\vec{\mu}(t) = 2\sum_{j=1}^{\text{occ}} \left\langle \phi_j(t) \middle| \vec{\mu}_{\text{op}} \middle| \phi_j(t) \right\rangle$ follows in a straightforward way from Eq. 1. Electric dipole polarizability and first hyperpolarizability are then easily extracted from the expansion, with the result (atomic units are used throughout this paper)

$$\alpha_{\lambda\mu}(\omega) = -2\sum_j^{\text{occ}} \sum_a^{\text{unocc}} P_{aj}^\lambda\left[U_{aj}^\mu(\omega) + U_{aj}^\mu(-\omega)\right] \tag{3}$$

$$\begin{aligned}\beta_{\lambda\mu\nu}(\omega,\omega') &= -4\sum_j^{\text{occ}} \sum_a^{\text{unocc}} P_{aj}^\lambda\left[U_{aj}^{\mu\nu}(\omega,\omega') + U_{aj}^{\mu\nu}(-\omega,-\omega')\right] \\ &\quad + 2\sum_{ij}^{\text{occ}} \sum_a^{\text{unocc}} P_{ij}^\lambda\left[U_{ai}^\mu(-\omega)U_{aj}^\nu(\omega') + U_{aj}^\mu(\omega)U_{ai}^\nu(-\omega')\right] \\ &\quad - 2\sum_j^{\text{occ}} \sum_{ab}^{\text{unocc}} P_{ab}^\lambda\left[U_{aj}^\mu(\omega)U_{bj}^\nu(-\omega') + U_{bj}^\mu(-\omega)U_{aj}^\nu(\omega')\right]\end{aligned} \tag{4}$$

Equations 3 and 4 provide expressions for the Cartesian components of the electric dipole polarizability and the first electric dipole hyperpolarizability tensors, respectively. $P_{rs}^\lambda \equiv -\left\langle \phi_r^{(0)} \middle| r_\lambda \middle| \phi_s^{(0)} \right\rangle$ is the (r,s) matrix element in the unperturbed MO basis set of the λ-th component of the electric dipole moment operator, $\vec{\mu}_{\text{op}} = -\vec{r}$. Equation 4 could actually be cast into a simpler form, according to the $2n+1$ rule [30]. Considering, however, the necessity of second-order perturbative corrections $\vec{U}^{AB}\left(\omega^A, \omega^B\right)$ to $\phi_j(t)$ for evaluating second hyperpolarizabilities, we have not exploited the $2n+1$ rule.

A glossary of the main NLO processes employed in measurements of hyperpolarizabilities can be found elsewhere (see, e.g., [3, 10, 11, 31]). Limiting ourselves to the quadratic response, we cite: (a) second-harmonic generation (SHG), as $\omega + \omega' = 2\omega$, i.e., the frequency-doubling effect caused by an incident laser beam of frequency ω [$\beta(-2\omega;\omega,\omega)$ is the usual notation for the corresponding hyperpolarizability]; (b) optical rectification, as $\omega + \omega' = 0$, $\omega \neq 0$ [associated hyperpolarizability $\beta(0;\omega,-\omega)$]; and (c) dc Pockels or quadratic electrooptic effect [$\beta(-\omega;\omega,0)$], the observed laser beam polarization change, quadratic in an applied electrostatic field. The static quadratic response corresponds obviously to $\omega = \omega' = 0$.

Expressions for the TDHF equations relative to the tensor amplitudes $\vec{U}_{rj}^A\left(\omega^A\right), \vec{U}_{rj}^{AB}\left(\omega^A, \omega^B\right)$ appearing in Eqs. 3 and 4 can be derived at the cost of some labor. As far as the present work is concerned, the formulation adopted allows one to approach the problem of the nonlinear e.m. response in full generality, avoiding its reduction to a set of answers for particular effects such as those listed above. The equations involved can be expressed compactly in terms of appropriate supermatrices and supervectors, as follows

$$\begin{aligned}[\mathbf{H}_1 + \omega\mathbf{1}]\mathbf{U}^\lambda(\omega) + [\mathbf{H}_1 - \omega\mathbf{1}]\mathbf{U}^\lambda(-\omega) &= -2\mathbf{P}^\lambda \\ [\mathbf{H}_2 + \omega\mathbf{1}]\mathbf{U}^\lambda(\omega) - [\mathbf{H}_2 - \omega\mathbf{1}]\mathbf{U}^\lambda(-\omega) &= \mathbf{0}\end{aligned} \tag{5}$$

$$\begin{aligned}&[\mathbf{H}_1 + (\omega + \omega')\mathbf{1}]\mathbf{U}^{\mu\nu}(\omega, \omega') \\ &\quad + [\mathbf{H}_1 - (\omega + \omega')\mathbf{1}]\mathbf{U}^{\mu\nu}(-\omega, -\omega') \\ &\quad = -\frac{1}{2}\mathbf{R}^{\mu\nu} \\ &[\mathbf{H}_2 + (\omega + \omega')\mathbf{1}]\mathbf{U}^{\mu\nu}(\omega, \omega') \\ &\quad - [\mathbf{H}_2 - (\omega + \omega')\mathbf{1}]\mathbf{U}^{\mu\nu}(-\omega, -\omega') \\ &\quad = -\frac{1}{2}\mathbf{S}^{\mu\nu}\end{aligned} \tag{6}$$

$\mathbf{H}_1$ and $\mathbf{H}_2$ are supermatrices whose elements, totally independent of the presence of external fields, can be written in the form

$$\begin{aligned}(\mathbf{H}_1)_{ai,bk} &= 4(ai|kb) - (ab|ki) - (ak|bi) + (\varepsilon_a - \varepsilon_i)\delta_{ab}\delta_{ki} \\ (\mathbf{H}_2)_{ai,bk} &= (ak|bi) - (ab|ki) + (\varepsilon_a - \varepsilon_i)\delta_{ab}\delta_{ki}\end{aligned} \tag{7}$$

involving two-electron integrals expressed in terms of MOs [$(i, k) \equiv$ occupied; $(a, b) \equiv$ unoccupied]. $\mathbf{1}$ is the identity supermatrix of proper dimensions. $\mathbf{P}^\lambda$ is a supervector with elements P_{aj}^λ (see Eqs. 3 and 4).

Analogously, $\mathbf{U}^{\lambda}(\pm\omega)$ is a supervector with elements $U^{\lambda}_{aj}(\pm\omega)$ associated with the various transitions $j \rightarrow a$. The solution of the coupled set of Eq. 5 solves completely the linear response problem. Considering that the dynamic electric-dipole polarizability $\vec{\alpha}(\omega)$, Eq. 3, is determined by the quantity $[\mathbf{U}^{\lambda}(\omega)+\mathbf{U}^{\lambda}(-\omega)]$ more than by $\mathbf{U}^{\lambda}(\omega)$ and $\mathbf{U}^{\lambda}(-\omega)$ separately, we have found it convenient in practice to work with the equation set

$$\left[\mathbf{H}_2\mathbf{H}_1 - \omega^2\mathbf{1}\right]\left[\mathbf{U}^{\lambda}(\omega) + \mathbf{U}_{\lambda}(-\omega)\right] = -2\mathbf{H}_2\mathbf{P}^{\lambda} \qquad (8)$$

which follows from Eq. 5 by simple manipulations.

The structure of the coupled equation set (Eq. 6) for the amplitudes $\mathbf{U}^{\mu\nu}(\omega,\omega')$ and $\mathbf{U}^{\mu\nu}(-\omega,-\omega')$ is similar to that of Eq. 5 for the linear response. The main difference lies in the inhomogeneities $\mathbf{R}^{\mu\nu}$ and $\mathbf{S}^{\mu\nu}$, a couple of supervectors with very complicated elements, involving among other things two-electron integrals and elements of the supervectors $\mathbf{U}^{\mu}(\pm\omega)$, $\mathbf{U}^{\nu}(\pm\omega)$. Even in this case, the coupled equations (Eq. 6) can be conveniently replaced by the equation set

$$\begin{aligned}&\left[\mathbf{H}_2\mathbf{H}_1 - (\omega+\omega')^2\mathbf{1}\right][\mathbf{U}^{\mu\nu}(\omega,\omega') + \mathbf{U}^{\mu\nu}(-\omega,-\omega')]\\ &\quad = \frac{1}{2}[(\omega+\omega')\mathbf{S}^{\mu\nu} - \mathbf{H}_2\mathbf{R}^{\mu\nu}] \qquad (9)\end{aligned}$$

as readily evinced from Eq. 4.

The supermatrices $\mathbf{H}_1$, $\mathbf{H}_2$ are identical to those involved in the RPA treatment of the same problem. More specifically, they should be compared with the combinations $\mathbf{A}+\mathbf{B}$ and $\mathbf{A}-\mathbf{B}$ of the supermatrices $\mathbf{A}$, $\mathbf{B}$ introduced by Rowe in his formulation of the RPA problem [14, 32]. This occurrence is obviously anything but unexpected, in view of the well-established equivalence between the TDHF and RPA approaches. With regard to this, our computer package takes some advantage from the inclusion of a routine where the RPA secular equation is diagonalized, so as to generate the totality of the transition energies. This is probably a much more efficient way for individuating the poles (here the response functions grow unlimitedly) compared with the search based on a scanning procedure where the whole range of frequencies is explored by small successive increments $\Delta\omega$ of the frequency.

Results

Static hyperpolarizability data

As already mentioned, our calculations concerning the molecules H_2O, CH_4, and NH_3 refer exclusively to the electronic contribution to the involved response functions (Born–Oppenheimer approximation, at the experimental equilibrium geometry). Although the primary interest of our investigation is directed to the first hyperpolarizability, results for the electric dipole polarizability will also be presented, in view of their obvious relevance.

Static property data for the three molecules are collected in Tables 1, 2 and 3, for H_2O, CH_4, and NH_3, respectively. For each molecular system we report several estimated values for the independent components of the tensors β (first dipole hyperpolarizability) and α (dipole polarizability), as obtained from different STO basis sets. S_{TRK} values calculated for the Thomas–Reiche–Kuhn sum-rule are also reported. Their deviation from the exact value of 10 is in some sense a measure of the completeness of the different basis sets employed. In addition to the independent components of β, the quantity $\bar{\beta} \equiv (3/5)\sum_{j=x,y,z}\beta_{zjj}$, often referred to as mean hyperpolarizability, with z the dipole moment axis [3, 9, 10, 11, 31], is also explicitly provided.

Comments concerning the connection between computed values of the observables and basis set characteristics, something very difficult to establish in general, are even more difficult in our case because of the paucity of the computational experience with STOs. This is not

Table 1. Static dipole polarizability and first dipole hyperpolarizability independent components of the H_2O molecule (in a.u.). The molecule (equilibrium geometry) lies in the (xz)-plane with the$z$-axis along the electric dipole

	DPA[a]	B1	B2	B3	B4	B5	B6	B7	LZ[b]	MA[c]	KSAY[d]	SB[e]	LAVJSH[f]
α_{xx}	7.592	8.956	8.959	8.961	9.124	9.216	9.223	9.204	9.033	9.179	9.180	9.164	9.19
α_{yy}	4.277	7.047	7.048	7.049	7.444	7.912	7.894	7.906	7.575	7.900	7.910	7.957	7.90
α_{zz}	6.160	7.945	7.947	7.949	8.215	8.472	8.524	8.521	8.271	8.522	8.515	8.526	8.53
$\bar{\alpha}$	6.010	7.983	7.985	7.986	8.261	8.533	8.547	8.544	8.293	8.534	8.535	8.55	8.54
S_{TRK}	10.403	9.821	9.820	9.818	9.840	9.905	9.905	9.921					
$-\beta_{xxz}$	8.986	9.488	9.530	9.568	9.719	9.257	9.602	9.076	10.581	9.40	9.359	9.4	9.47
$-\beta_{yyz}$	−0.128	−1.931	−1.927	−1.921	−0.993	0.366	1.404	1.605	−1.098	1.35	1.244	1.4	1.30
$-\beta_{zzz}$	7.575	2.894	2.923	2.953	3.948	4.893	7.580	7.725	3.574	7.71	7.288	7.1	7.83
$-\bar{\beta}$	9.861	6.270	6.316	6.414	7.605	8.710	11.151	11.044	7.834	11.07	10.735	10.8	11.46

B1 (51) = DPA + $3p_O$ (2.90) + $3p_O$ (1.718) + $3d_O$ (1.30) + $2p_H$ (1.30)
B2 (54) = B1 + $2p_O$(0.4295)
B3 (57) = B2 + $2p_O$(0.71575)
B4 (63) = B3 + $2s_O$ (0.318) + $3d_O$ (0.636) and substitution of $3d_O$ (1.30) with $3d_O$ (1.061)
B5 (70) = B4 + $2s_O$ (0.5305) + $2s_O$ (1.0) + $3d_O$ (1.8)
B6 (77) = B5 + $4f_O$ (0.9)
B7 (83) = B6 + $3p_H$ (0.928)

[a] Ref. 33

[b] Lazzeretti P, Zanasi R (1981) J Chem Phys 74:5216

[c] Maroulis G (1998) Chem Phys Lett 289:403

[d] Ref. 12

[e] Ref. 8

[f] Ref. 9

Table 2. Static dipole polarizability and first dipole hyperpolarizability independent components of the CH_4 molecule (in a.u.). Molecule in its equilibrium geometry

	B1	B2	B3	B4	B5	B6	B7	LZ[a]	MA[b]	SB[c]	BGC[d]
α_{xx}	12.339	12.677	14.248	14.598	15.132	16.249	16.364	15.120	15.98	12.985	15.889
S_{TRK}	10.423	10.591	10.263	10.181	10.255	10.009	10.576				
$-\beta_{xyz}$	2.200	1.201	−0.056	−0.321	−0.160	12.684	12.735	19.712	11.10	5.906	10.918

B1 (39) = $1s_C$ (5.1, 9.1),$2s_C$ (1.3, 2.3), $3s_C$ (6.1), $2p_C$ (6.1, 1.1, 1.8), $3d_C$ (1.3), $1s_H$ (1.39), $2s_H$ (2.1), $2p_H$ (1.8)
B2 (42) = B1 + $3p_C$ (2.1)
B3 (45) = B1 + $3s_C$ (1.7) + $3d_C$ (1.7)
B4 (48) = B3 + $3p_C$ (2.3)
B5 (54) = B4 + $3s_C$ (1.1) + $3d_C$ (1.1)
B6 (70) = B5 + $2s_H$ (1.75) + $2p_H$ (1.0)
B7 (77) = B4 + $4f_C$ (1.1) + $2s_H$ (1.0) + $2p_H$ (1.0)

[a] Lazzeretti P, Zanasi R (1981) J Chem Phys 74:5216
[b] Maroulis G (1994) Chem Phys Lett 226:420
[c] Ref. 13
[d] Ref. 38

to say, of course, that the problem of selecting adequate basis sets in the Gaussian case is simple (for a concise review, see for example [11]). The construction of a good, finite basis set, for use in quantum chemistry calculations addressed to NLO applications, remains in every case a piece of mastery.

There are only a few indications about the requisites a good-quality basis set, which should reasonably have to: (i) yield a rather accurate energy estimate; (ii) include from several to many extra, diffuse functions, so as to span not only the valence region, but also the outermost region of the molecule; and (iii) verify as well as possible sum-rule and gauge-invariance [14] constraints attesting the degree of the basis completeness. Requirements like these can hardly be regarded as providing strong criteria. In our opinion, hope for effectively constructive recipes is probably utopian.

The data reported in Table 1 for H_2O will be discussed rather diffusely, trying to put in evidence features related to the various basis sets utilized. All the basis sets elaborated share a 34 STO "core", constituted by a basis set proposed many years ago by Dunning et al. [33] to generate a near H–F wavefunction for the molecule. Starting from this core basis set (label DPA), all the other ones have been constructed by a progressive augmentation/verification procedure, until reaching the largest size considered adequate (83 STOs). The examples provided in Table 1 actually correspond only to a subset of a much larger number of basis set experiments. Polarization STOs have progressively been added to the DPA basis until B1 was generated, a basis set of only slightly larger size compared to that utilized by us in a previous study of the same molecule [34]. The basis sets from B2 to B7 follow from B1 by partial application of a "decoration" procedure allowing the generation of polarization STOs, along the lines suggested originally by Sadlej [35] and reconsidered later by us (criterion B of ref. [36]).

Although the emphasis of this paper is on computational features of the nonlinear e.m. response of molecules, we cannot refrain from extending our considerations to the linear response, because of obvious motivations of relevance, not least the fact that the basis set selection can hardly get rid of how the dipole polarizability behaves.

Extremely significant changes of the polarizability components go along with the basis augmentation from DPA (34) to B1 (51), the changes amounting to 20, 65, and 30% for α_{xx}, α_{yy}, and α_{zz}, respectively. The changes caused in the same properties as a consequence of further basis augmentation from B1 to B7 (83) are more moderate (with the exception of α_{yy}) and amount to 3, 12, and 7%. STOs on the oxygen atom associated with azimuthal quantum number $l = 3$ do not seem to play an important

Table 3. Static dipole polarizability and first dipole hyperpolarizability independent components 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

	B1	B2	B3	B4	B5	B6	B7	LZ[a]	MA[b]	RH[c]	KSAY[d]	SB[e]
α_{xx}	13.188	13.125	12.925	12.919	12.945	12.949	12.940	12.733	12.76	12.73	12.776	12.768
α_{zz}	12.949	13.183	13.319	13.497	13.554	13.555	13.483	13.244	13.25	13.29	13.324	13.347
$\bar{\alpha}$	13.108	13.144	13.056	13.112	13.148	13.151	13.121	12.903	12.92	12.92	12.959	12.96
S_{TRK}	9.126	9.628	9.617	9.633	9.681	9.683	9.758					
β_{xxx}	−10.599	−10.584	−9.707	−9.821	−9.567	−9.419	−9.544	−8.930	−8.93	−8.86	−8.665	
β_{zxx}	12.219	12.295	9.363	8.830	8.226	8.158	8.242	6.840	7.39	7.54	7.293	7.0
β_{zzz}	20.062	13.132	−7.715	−0.857	6.860	7.095	9.032	7.758	12.74	8.79	11.674	11.1
β	27.035	22.634	6.607	10.082	13.988	14.047	15.310	12.863	16.51	14.32	15.756	15.1

B1 (48) = $1s_N$ (8.5, 6.0),$2s_N$ (2.3, 1.4), $2p_N$ (6.0, 2.0, 1.3), $3p_N$ (0.5), $3d_N$ (1.0), $1s_H$ (0.9, 1.25), $2s_H$ (2.32), $2p_H$ (1.15, 0.8)
B2 (53) = B1 + $4d_N$ (1.2)
B3 (59) = B2 + $2p_N$ (0.575) + $3p_N$ (0.92)
B4 (64) = B3 + $2s_N$ (0.5) + $3s_N$ (0.8) + $2p_N$ (0.35)
B5 (73) = B4 + $2p_H$ (1.25) and substitution of $2p_H$ (0.8) with $2p_H$ (0.7)
B6 (80) = B5 + $4f_N$ (0.4)
B7 (83) = B6 + $2p_N$ (8.5)

[a] Lazzeretti P, Zanasi R (1981) J Chem Phys 74:5216
[b] Maroulis G (1992) Chem Phys Lett 195:85
[c] Ref. 2
[d] Ref. 12
[e] Ref. 8

role. An excursion among the various cases shows that the TRK sum-rule is reasonably well verified and the dipole moment (values not reported) is stable at the value $\mu_z = 0.777$ a.u. Following in the same way the behavior of the hyperpolarizability components, we discover that, due to the basis augmentation from DPA to B1, β_{xxz}, β_{yyz}, β_{zzz} manifest a not dissimilar behavior compared to α_{xx}, α_{yy}, α_{zz}. In particular, β_{yyz} suffers an enormous percentage change, from 0.13 to 1.93 a.u. Further augmentation of the basis set, from B1 to B7, leads to more stabilized values for the β components, even though the permanence of somewhat erratic behavior is evident. Contrary to the polarizability case, here the inclusion in the basis of STOs with $l = 3$ is beneficial and important, particularly for the components β_{yyz} and β_{zzz}. β_{yyz}, moreover, stabilizes its negative sign thanks to this basis set augmentation. The comparison values reported agree very well with ours as far as the polarizability is concerned, while the accordance in the hyperpolarizability case is only good, attesting to the great difficulty of reaching manifestly converged results, in line with the general expectation and previous comments concerning the delicate nature of this observable [8].

Static-property data for CH_4 are collected in Table 2. Since organization of the table and procedures used for generating the various basis sets utilized do not differ from those of Table 1, we can proceed a bit more quickly in our comments. The core (B1) shared by all the basis sets considered involves a subset of 39 STOs and is the same basis used in an old study of the molecule by two of the present authors [37]. A rich decoration of this core through addition of polarization functions at the central atom leads progressively to the basis set B5 (54). By further augmentation of this basis, in terms of STOs centered at the H atoms, we attain B6 (70) and finally B7 (77), the largest size investigated in this case.

The augmentation B1 → B5 leads to a very marked change (+23%) of the dipole polarizability and shifts the TRK sum-rule value in the right way, while the only nonvanishing component β_{xyz} of the first dipole hyperpolarizability jumps from -2.20 a.u. to $+0.16$ a.u. After further augmentation from B5 to B6, the resulting dipole-polarizability change is still important (+7%) and the sum-rule is verified almost perfectly, while β_{xyz} recovers the initial negative sign, becoming large in absolute value. The final augmentation B6 → B7 reported, corresponding to the addition of a complete subset of STOs with $l = 3$ on the central atom, leaves both polarizability and hyperpolarizability essentially unmodified, while the sum-rule result deviates from 10 to a large extent.

Our predictions for the static properties of NH_3 are reported in Table 3. Although the organization of the table is identical to that of the previous two, the basis set experimentation setup is somewhat different. Contrary to the cases of H_2O and CH_4, where the elaboration of the various basis sets proceeds by augmentation of a STO subset (core) suggested by preceding computational experience, here the starting basis set B1 has been generated with relatively modest attention paid to its quality from the energy point of view, stressing sooner its effectiveness in describing electric linear response properties (polarizability). This implies, of course, that some work (not reported) stays actually behind B1.

After this premise, it should be no surprise that estimates of the polarizability components α_{xx}, α_{zz} are very good at the very outset (B1) and remain essentially stable during the experimentation in terms of the various basis sets explored, with the TRK sum-rule value progressively shifting toward the correct electron number (10). As expected, however, the hyperpolarizability situation is not as favorable: β_{xxx} and β_{xxz} change in an acceptably smooth manner, becoming reasonably stabilized at the end, but β_{zzz} displays fluctuating behavior, with sign changes, failing the goal of a clear convergence. This behavior offers a particularly clear indication of the specific character of the nonlinear-response problem investigated, that is hardly identifiable with that posed by a seemingly proximate observable such as polarizability.

How our findings compare with those of independent TDHF (RPA) calculations is a significant element for assessing the quality of our results. The inspection of Tables 1, 2 and 3 puts in evidence that static polarizabilities are at the very least in good agreement (but the accordance is more often extremely or very good), whereas for hyperpolarizabilities the story is a bit different. The very delicate nature of this observable reflects itself in predictions that in general can only be regarded as being in substantial agreement, because of the permanence of rather erratic fluctuations. These fluctuations manifest themselves principally at the level of single components, while in this respect $\bar{\beta}$ exhibits much better accordance.

Hyperpolarizability and frequency dependence

As already remarked elsewhere [8, 10], the dependence of the hyperpolarizabilities on the frequencies of the e.m. fields interacting with the molecule is, along with basis set choice, electron correlation appraisal, and vibrational corrections, the fourth element to be considered in a computational context before accurate ab initio estimates can be put forward. Even though the TDHF predictions discussed in this paper cannot surely be regarded as accurate, some attention to the dispersion effects, related to the oscillating nature of the externally applied electric fields, must nevertheless be paid. In the first place, in fact, most measurements of the hyperpolarizabilities are based on experiments involving optical processes. On the theoretical-computational side, moreover, frequency-dependent hyperpolarizabilities evaluated at a lower level of theory (such as TDHF) can be exploited to approximately estimate the dispersion effects of higher-level approaches (“percentage corrections” [8, 10]).

Dynamic polarizability and hyperpolarizability data of H_2O, CH_4, and NH_3 are collected in Tables 4, 5 and 6, respectively. With the exception of CH_4, where two different wavelengths have been tested ($\lambda = 694.3$ and 760 nm), only dispersion effects at the wavelength $\lambda = 694.3$ nm were probed. The exploration of the dispersion effects at $\lambda = 694.3$ nm (corresponding to $\omega = 0.0656$ a.u.) is now a standard practice in computational studies of hyperpolarizabilities, a consequence of availability of experimental SHG data at such a wavelength.

A simple glance at the contents of Tables 4, 5 and 6 shows that only estimates from a single basis set have been reported, the chosen basis set corresponding to the largest one elaborated by us in each case. The entries collected in the tables refer to independent polarizability and hyperpolarizability components. In particular, for H_2O and NH_3, SHG $\beta(-2\omega;\omega,\omega)$ data and dc Pockels $\beta(-\omega;\omega,0)$ data are explicitly considered, according to a common practice, along with average values $\bar{\beta}(-2\omega;\omega,\omega)$, $\bar{\beta}(-\omega;\omega,0)$, in order to favor comparisons with other calculations and possible experiments.

The polarizability changes relative to the static values, clearly rather small in all cases, conform with expectation. The modest increase observed can be traced back to the fact that, at the imposed frequency, the molecular response is characterized by normal dispersion. The accordance with independent calculations is excellent for H_2O and NH_3. For CH_4, we agree closely with calculations reported by Bishop et al. ($\lambda = 760$ nm) [38], but disagree with respect to older estimates put forward by Sekino et al. [13] at $\lambda = 694.3$ nm, in analogy to the behavior displayed by the static observable (see previous subsection).

Moving to the hyperpolarizability case, for CH_4 the comparison of our findings with those of Bishop et al. [38] is good for both $\beta_{xyz}(-\omega;\omega,0)$ and $\beta_{xyz}(-2\omega;\omega,\omega)$ ($\lambda = 760$ nm), while very large discrepancies with respect to Sekino et al. [13], at $\lambda = 694.3$ nm, are to be pointed out, a likely consequence of basis set inadequacy. As a further comment, we remark that larger changes compared to those characterizing the polarizability are observed, in line with the fact that dispersion effects are larger in the case of processes involving a dynamic perturbation of higher order [13].

Table 4. Dipole polarizability and first dipole hyperpolarizability of the H_2O molecule (in a.u.) at $\lambda = 694.3$ nm: results for two NLO processes (SHG and dc Pockels effects)

	B7	KSAY[a]	SB[b]	Expt.[c]
$\alpha_{xx}(\omega)$	9.261	9.271	9.1645	
$\alpha_{yy}(\omega)$	8.024	8.028	7.9569	
$\alpha_{zz}(\omega)$	8.623	8.616	8.5264	
$\bar{\alpha}(\omega)$	8.636	8.639	8.55	
$\beta_{xxz}(-\omega;\omega,0)$	−9.430	−9.716		
$\beta_{yyz}(-\omega;\omega,0)$	−1.910	−1.525		
$\beta_{zxx}(-\omega;\omega,0)$	−9.440	−9.723		
$\beta_{zyy}(-\omega;\omega,0)$	−1.709	−1.326		
$\beta_{zzz}(-\omega;\omega,0)$	−8.144	−7.682		
$\bar{\beta}(-\omega;\omega, 0)$	−11.614		−11.290	
$\beta^{K}(-\omega;\omega,0)$	−11.519	−11.172		
$\beta_{xxz}(-\omega;\omega,\omega)$	−10.214	−10.505		
$\beta_{yyz}(-\omega;\omega,\omega)$	−2.471	−2.029		
$\beta_{zxx}(-\omega;\omega,\omega)$	−10.259	−10.540		
$\beta_{zyy}(-\omega;\omega,\omega)$	−1.713	−1.276		
$\beta_{zzz}(-\omega;\omega,\omega)$	−9.095	−8.579		
$\bar{\beta}(-2\omega;\omega,0)$	−12.925	−12.524	−12.568	−22.0 ± 0.9

[a] Ref. 12
[b] Ref. 8
[c] Ref. 10

Table 5. Dipole polarizability and first dipole hyperpolarizability of the CH_4 molecule (in a.u.) at $\lambda = 694.3$ nm and $\lambda = 760$ nm: results for two NLO processes (SHG and dc Pockels effects)

	$\lambda = 694.3$ nm		$\lambda = 760$ nm	
	B7	SB[a]	B7	BGC[b]
$\bar{\alpha}(\omega)$	16.597	12.815	16.558	16.073
$\beta_{xyz}(-\omega;\omega,0)$	−13.356	−6.648	−13.251	−11.415
$\beta_{xyz}(-2\omega;\omega,\omega)$	−14.744	−6.971	−14.383	−12.517

[a] Ref. 8
[b] Ref. 38

For H_2O and NH_3, the validity of the latter remark appears confirmed. As already mentioned, only dispersion effects at $\lambda = 694.3$ nm have been reported in the present paper for these molecules, to be comparable with independent estimates. In the case of H_2O, good agreement with Kobayashi et al. [12] can be noticed for the single components of both $\beta(-\omega;\omega,0)$ and $\beta(-2\omega;\omega,\omega)$, the accordance for $\bar{\beta}(-\omega;\omega,0)$ and $\bar{\beta}(-2\omega;\omega,\omega)$ becoming even excellent. For NH_3, the situation is not very dissimilar. At the level of comparison of the single components of both $\beta(-\omega;\omega,0)$ and $\beta(-2\omega;\omega,\omega)$, the accordance with the estimates from independent calculations (same level of theory) can be considered only good. On the other hand, the average values $\bar{\beta}(-\omega;\omega,0)$

Table 6. Dipole polarizability and first dipole hyperpolarizability of the NH_3 molecule (in a.u.) at $\lambda = 694.3$ nm: results for two NLO processes (SHG and dc Pockels effects)

	B7	KSAY[a]	SB[b]	SLAJ[c]	Expt.[d]
$\alpha_{xx}(\omega)$	13.112	12.944	12.768		
$\alpha_{zz}(\omega)$	13.811	13.645	13.347		
$\bar{\alpha}(\omega)$	13.345	13.178	12.96		
$\beta_{xxx}(-\omega;\omega,0)$	−10.000				
$\beta_{xxz}(-\omega;\omega,0)$	8.866	7.847			
$\beta_{zxx}(-\omega;\omega,0)$	9.010	7.963			
$\beta_{zzz}(-\omega;\omega,0)$	10.760	13.421			
$\bar{\beta}(-\omega;\omega,0)$	17.210	17.562	16.740		
$\beta^{K}(-\omega;\omega,0)$	17.354	17.678			
$\beta_{xxx}(-2\omega;\omega,0)$	−11.033				
$\beta_{xxz}(-2\omega;\omega,0)$	10.542	9.328		9.47	
$\beta_{zxx}(-2\omega;\omega,\omega)$	11.248	9.916		10.03	
$\beta_{zzz}(-2\omega;\omega,\omega)$	15.620	18.256		17.76	
$\bar{\beta}(-2\omega;\omega,\omega)$	22.304	22.383	21.978	22.24	48.4 ± 1.2

[a] Ref. 12
[b] Ref. 8
[c] Spirko V, Luo Y, Ågren H, JørgensenP (1993) J Chem Phys 99:9815
[d] Ward JF, Miller CK (1979) Phys Rev A 19:826

and $\bar{\beta}(-2\omega;\omega,\omega)$ display very good agreement, as a result of compensation mechanisms. The $\beta^K(-\omega;\omega,0)$ quantities, combinations of appropriate components of $\beta(-\omega;\omega,0)$ measured in Kerr-type experiments [31], display an analogous behavior and compare very well with the findings of other sources [12]. It is useless to say that TDHF estimates and experiments are very far from each other, a clear sign of manifold inadequacies at the level of theoretical/computational performance (surely) and experiments (probably).

Conclusions

The possible role of STO basis sets for ab initio predictions of the e.m. nonlinear response (first hyperpolarizability) of molecular systems has been investigated on three small polyatomics (H_2O, CH_4, NH_3), in terms of a coupled SCF procedure (TDHF). The results obtained strengthen the evidence that the evaluation of NLO properties, even in the approximation of neglecting correlation effects, is a problem other than that posed to quantum chemists by linear-response property studies. The necessity of extending considerably the basis set size beyond that demanded for assuring convergent results in the case of electric polarizability is further ascertained, along with the certainty that the computational task remains hard, even though use of STOs can mitigate this difficulty, reducing the basis extensions typically required by Gaussian calculations to achieve comparable results. More will be reported on this subject after developing further experimentation on the basis of the present results, mainly those obtained in the case of NH_3, which could suggest the effectiveness of different strategies.

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