FULL PAPER

Accurate Calculations of Dynamic First Hyperpolarizability: Construction of Physically Justified Slater-Type Basis Sets

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An efficient procedure for construction of physically rationalized Slater-type basis sets for calculations of dynamic hyperpolarizability is proposed. Their performance is evaluated for the DFT level calculations for model molecules, carried out with a series of functionals. Advantages of new basis sets over stand-

Introduction

Significant progress in development of laser technology and constantly growing requirements for new materials with specific nonlinear optical (NLO) properties has been observed in the last few decades. This resulted in recent advances in development of new generations of optical devices and significant increase of experimental and theoretical investigation of NLO properties of chemical compounds.^[1] Frequency-dependent first hyperpolarizability is one of the challenging NLO properties, which could be measured experimentally only indirectly, based on temperature dependence of the third-order hyperpolarizability of investigated species. For accurate theoretical evaluation of the first hyperpolarizability, one has to use approaches with a carefully balanced treatment of all important contributions, to avoid subtle cancellations of different vital contributions.^[1] Up to data CC3 model^[2,3] derived from Coupled Cluster family of quantum chemical techniques, in combination with doubly-augmented (d-aug-cc-pVXZ) basis sets is considered to be the most accurate approach for calculation of the first hyperpolarizability.^[4,5]

For large molecules where computational cost of calculations at the CC level plays a critical role, a selection of optimal by size, and at the same time physically adapted basis set is a challenging task.

The well-known solution to this problem is an "extension" of the initial basis set of atomic orbitals (AOs) used in calculations. A conventional way of such an "extension" involves the increase of the numbers of original AOs by means of augmentation of the so-called polarization and diffuse functions to the initial set of AOs. However, in such a case, the size of the basis set obtained exceeds considerably the initial basis set size. In addition, neither the required number of additional functions, nor the functional form of such functions is defined by any physically justified manner.

The POL sets^[6–8] were especially developed for calculations of molecular electric properties. These sets were obtained through addition of polarization functions to a source set of Gaussian-type functions, exploiting a model of harmonic oscillator in external homogeneous static electric field.^[9] This ard d-aug-cc-pVTZ and recently developed LPOL-(FL,FS) Gaussian-type basis sets are discussed. © 2014 Wiley Periodicals, Inc.

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model was later generalized to the case of dynamic electric field,^[10] leading to development of the reduced-size polarized ZPOL^[11-13] and the large polarized LPOL-n (n = DS, DL, FS, and FL)^[14] basis sets. The first were developed for moderately accurate calculations of static polarizabilities in large systems, whereas the latter were intended for accurate studies of linear and nonlinear molecular electric properties.

The D-type basis sets contain only the first-order polarization functions, whereas in the F-type sets both the first- and the second-order polarization functions are present. The "S" and the "L" in the LPOL-n sets' name stand for "small" and "large," respectively, and reflect the difference in the number of first- and second-order contracted Gaussian-type orbitals.

There is not much development of this kind for Slater-type orbitals (STOs). In recently standard basis set of valence, triplezeta STOs for the second period atoms has been augmented by two diffuse 4s,3p,3d, and 4f functions.^[15] The principal quantum numbers and orbital exponents of such functions have been fitted based on overlap matrix minimization. Field-induced polarization (FIP) functions obtained by the approximation of asymptotic behavior of the highest occupied orbital have been proposed initially^[16] and optimized for H—Kr atoms.^[17] The obtained functions significantly improve the

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accuracy of calculated response properties. Recently, Carmona-Espindola et al. developed a new approach for the calculation of static and dynamic hyperpolarizabilities. Such approach incorporated in the framework of auxiliary density perturbation theory, in combination with Gaussian-type TZVP-FIP1 basis set and GEN-A2* auxiliary functions in most cases shows good agreement with experimental data and the results of CCSD level calculations.^[18]

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The FIP Gaussian-type functions also used in the aug-pc-n (n = 1, 2) basis sets developed by Jensen,^[19–22] and the property-optimized sets of Rappoport and Furche.^[23] The latter were recently built on the Karlsruhe segmented contracted basis sets of split-valence to quadruple-zeta valence quality^[24] and optimized variationally for the evaluation of polarizabilities.

Here we recommend the approach for development of physically justified basis sets of Slater-type AO for calculations of dynamic hyperpolarizability. Our proposal is based on solution of the nonhomogeneous Schrödinger equation for the model problem "one-electron atom in an external uniform field," using the closed representation of the Green's function.^[25,26] The efficiency of this approach has been confirmed earlier for construction of basis sets for calculations of nuclear magnetic shielding,^[27–31] spin–spin coupling constants,^[32]magnetic susceptibility,^[33–35] polarizability,^[34,35] and vibrational frequencies.^[36] The performance of the obtained basis sets on the dynamic hyperpolarizability calculations at DFT levels has been tested here for the series of inorganic and organic molecules.

Theory

As initial basis set we have chosen a set of STOs. Such orbitals provide more accurate description of wave function compared to Gaussian-type orbitals, due to coincidence of asymptotic behavior of STO and hydrogen wave function in peripheral regions of configuration space.

First, we need to consider the problem of "hydrogen-like atom in external uniform electric field." First-order correction function $\chi^{[1]}$ for unperturbed STO $\chi^{(0)}$ corresponds to solution of nonhomogeneous Schrödinger equation

$$\left[-\frac{1}{2}\Delta + V(r) - E\right]\chi^{(1)}(r) = \hat{\lambda}W(r)\chi^{(0)}(r),$$
(1)

and could be expressed as:

$$\chi^{(1)}(\mathbf{r}) = \int G_{E}(\mathbf{r}, \mathbf{r}') \widehat{W}(\mathbf{r}') x^{(0)}(\mathbf{r}') d\mathbf{r}'.$$
 (2)

where V(r)—potential energy operator, which determines type of AO, $\hat{W}(r)$ —perturbation operator, $G_E(\mathbf{r}, \mathbf{r'})$ —Green's function which corresponds to homogeneous Eq. (1).

For the spherically symmetrical potential V(r), the Green's function can be expressed in the following form

$$G_{E}(\mathbf{r},\mathbf{r}') = \sum_{l,m} g_{l}(r,r';E) Y_{lm}(r_{0}) Y_{lm}^{*}(r'_{0})$$
(3)

where Y_{lm} are spherical functions of the argument $r_0 = r/r$, and $g_l(r,r'; E)$ represents radial part of the Green's function.

Using Green's function method, we have obtained^[37,38] analytical expressions of the target first-order correction functions for Slater-type AO in electric field (with perturbation operator $\hat{W}_{z}(r) = -r \cos\theta$):

$$1s^{(1)} = -\frac{\xi_{1}^{-3/2}}{\sqrt{3}}e^{-\rho}\rho(2+\rho)Y_{10}$$

$$2s^{(1)} = \frac{\xi_{2}^{-3/2}}{6\sqrt{2}}e^{-\rho/2}\rho(30-\rho^{2})Y_{10}$$

$$2p_{x,y}^{(1)} = -\frac{\xi_{2}^{-3/2}}{2\sqrt{30}}e^{-\rho/2}\rho^{2}(6+\rho)\begin{cases}Y_{21}\\Y_{21}^{s}\end{cases}$$

$$2p_{z}^{(1)} = -\frac{\xi_{2}^{-3/2}}{3\sqrt{2}}e^{-\rho/2}\left[\left(\frac{\rho^{3}}{2}-3\rho^{2}-3\rho+6\right)Y_{00}+\frac{1}{\sqrt{5}}(\rho^{3}+6\rho^{2})Y_{20}\right]$$
(4)

In Eq. (4) $\rho = \xi_i r$, and $Y_{lm}^{c,s}$ represent real spherical functions. Expressions for other components could be obtained in the same way as discussed above.^[35]

As could be seen from Eq. (4), the first-order correction functions could be expressed as linear combination of new STOs of specified type and quantity.^[34] Required in this stage correction of principal quantum number could be taken into account with scaling factor calculated using Eq. (5), which is based on the assumption of nuclei constancy

$$\xi_{\rm new} = n_{\rm old} \cdot \xi_{\rm old} / n_{\rm new} \,, \tag{5}$$

where "old" and "new" correspond to principal quantum number and orbital exponent for unperturbed and induced STOs, respectively.

It should be noted that in contrast to the approach described,^[39] the here proposed procedure does not require additional optimization of orbital exponents.

From Eq. (4), taking into account (5), the following expansion into a series^[40] could be obtained:

$$1s^{(1)}(\xi_{1}) \rightarrow \left[2p\left(\xi_{1} \cdot \frac{1}{2}\right)\right] + 3p\left(\xi_{1} \cdot \frac{1}{3}\right)$$

$$2s^{(1)}(\xi_{2}) \rightarrow 4p\left(\xi_{2} \cdot \frac{1}{2}\right) + \left[2p(\xi_{2})\right]$$

$$2p^{(1)}(\xi_{2}) \rightarrow \left[1s\left(\xi_{2} \cdot 2\right) + 3s\left(\xi_{2} \cdot \frac{2}{3}\right) + 3d\left(\xi_{2} \cdot \frac{2}{3}\right)\right]$$

$$+4d\left(\xi_{2} \cdot \frac{1}{2}\right) + 4s\left(\xi_{2} \cdot \frac{1}{2}\right)$$
(6)

As STOs contain only the highest degree of radius-vector expansion the terms in the brackets in expressions (6) could be neglected. Adding the remaining expansion terms to initial STO basis set, the following adapted basis set could be obtained:





$$\begin{cases} 1s(\xi_1), 2s(\xi_2), 2p(\xi_2), 3p\left(\xi_1 \cdot \frac{1}{3}\right), 4s\left(\xi_2 \cdot \frac{1}{2}\right), \\ 4p\left(\xi_2 \cdot \frac{1}{2}\right), 4d\left(\xi_2 \cdot \frac{1}{2}\right) \end{cases}$$
(7)

Basis set (7) which has been preliminary expanded in terms of primitive Gaussian-type orbitals according to the previous works,^[41-43] denoted as STO^{##-3G}_{el}, has been successfully applied^[35] for calculations of polarizability of organic molecules. In recent Kupka and coworkers' papers,^[44,45] this basis, as well as a basis STO^{##-3G}_{mag} used in determining wide spectrum of molecular properties and has demonstrated their effectiveness. As could be seen from (7), the notable feature of constructed Slater-type basis set for hydrogen atom is that it consists of just one basis function 1s of the ground state and its augmentation by 3p AO does not allow to describe the exited state of the atom. In this case, one can logically continue the procedure of obtaining of addition basis functions using explicit expression for the second-order correction function of perturbation theory, obtained, for example, in Refs. [16] and [46].

Second-order corrections to $1s^{(2)}$ could be expressed as following linear combination of STOs AO, induced by electric field:

$$1s^{(2)}(\xi_{1}) \rightarrow 5s\left(\xi_{1} \cdot \frac{1}{5}\right) + 4s\left(\xi_{1} \cdot \frac{1}{4}\right) + 3s\left(\xi_{1} \cdot \frac{1}{3}\right) + 5d\left(\xi_{1} \cdot \frac{1}{5}\right) + 4d\left(\xi_{1} \cdot \frac{1}{4}\right) + 3d\left(\xi_{1} \cdot \frac{1}{3}\right),$$
(8)

which allows to construct a new basis set for hydrogen atom as following:

$$1s(\xi_{1})3s\left(\xi_{1}\cdot\frac{1}{3}\right)4s\left(\xi_{1}\cdot\frac{1}{4}\right)5s\left(\xi_{1}\cdot\frac{1}{5}\right)3p\left(\xi_{1}\cdot\frac{1}{3}\right)$$

$$3d\left(\xi_{1}\cdot\frac{1}{3}\right)4d\left(\xi_{1}\cdot\frac{1}{4}\right)5d\left(\xi_{1}\cdot\frac{1}{5}\right),$$
(9)

In the same way, expansions for the second-order correction functions for unperturbed 2s, 2p, 3s, and 3p STOs of nonhydrogen atoms could be obtained:

$$2s^{(2)}(\xi_{2}) \rightarrow 6s\left(\frac{1}{3} \cdot \xi_{2}\right) + 5s\left(\frac{2}{5} \cdot \xi_{2}\right) + 4s\left(\frac{1}{2} \cdot \xi_{2}\right) + 6d\left(\frac{1}{3} \cdot \xi_{2}\right) + 5d\left(\frac{2}{5} \cdot \xi_{2}\right) + 4d\left(\frac{1}{2} \cdot \xi_{2}\right),$$

$$2p^{(2)}(\xi_{2}) \rightarrow 6p\left(\frac{1}{3} \cdot \xi_{2}\right) + 5p\left(\frac{2}{5} \cdot \xi_{2}\right) + 4p\left(\frac{1}{2} \cdot \xi_{2}\right) + 6f\left(\frac{1}{3} \cdot \xi_{2}\right) + 5f\left(\frac{2}{5} \cdot \xi_{2}\right) + 4f\left(\frac{1}{2} \cdot \xi_{2}\right),$$

$$3s^{(2)}(\xi_{3}) \rightarrow 7s\left(\frac{3}{7} \cdot \xi_{3}\right) + 6s\left(\frac{1}{3} \cdot \xi_{3}\right) + 5s\left(\frac{2}{5} \cdot \xi_{3}\right) + 7d\left(\frac{3}{7} \cdot \xi_{3}\right) + 6d\left(\frac{1}{3} \cdot \xi_{3}\right) + 5d\left(\frac{2}{5} \cdot \xi_{3}\right),$$

$$3p^{(2)}(\xi_{3}) \rightarrow 7p\left(\frac{3}{7} \cdot \xi_{3}\right) + 6p\left(\frac{1}{3} \cdot \xi_{3}\right) + 5p\left(\frac{2}{5} \cdot \xi_{3}\right) + 7f\left(\frac{3}{7} \cdot \xi_{3}\right) + 6f\left(\frac{1}{3} \cdot \xi_{3}\right) + 5f\left(\frac{2}{5} \cdot \xi_{3}\right),$$

$$(10)$$

expanded in terms of primitive Gaussian-type orbitals.^[41-43]

New STOs from right parts of Eq. (10) could be partially or completely used for improvement of $STO^{##}-3G_{el}$ basis set (7). Thus, basis set $STO^{##}(II)-3G_{el}$ includes basis set $STO^{##}-3G_{el}$ (7), all additional orbital sets from (10) for valence AO of non-hydrogen atoms, and basis set (9) for hydrogen atoms. Basis set $STO^{##}(IIS)-3G_{el}$ consists of $STO^{##}-3G_{el}$ basis set (7), one set of addition s- and p- orbitals from (10) with the same symmetry as unperturbed valence orbitals of non-hydrogen atoms, and one set of additional s-orbitals on hydrogen. The explicit form of proposed bases here may be found in Supporting Information. The "-S" name stand for "short". It should be noted that we have taken into account only correction functions for valence orbitals, as perturbation operator in this case represents operator of dipole moment, which contributes mainly in far-regions of configuration space.

The proposed approach provides also procedure for improvement of additional orbitals. In such cases, the renormalization procedure for the expansion coefficients of STOs for the primitive Gaussians is applied according to new values of orbital exponents (5) and altered quantum numbers n and l.

To our best knowledge, calculations of dynamic hyperpolarizability of organic molecules using Slater-type basis sets have not been performed so far.

Performance of Proposed Basis Sets

The performance of constructed STO^{##}(II)-3G_{el} and STO^{##}(IIS)-3G_{el} basis sets in comparison with d-aug-cc-pVTZ and LPOL-n (n = FL,FS) basis sets is illustrated by the results of the test calculations of the first dynamic hyperpolarizability tensors for the set of HF, H₂O, NH₃, CO, CH₃CN, CH₃F, and NO molecules with number of DFT functionals (B3PW91, B3P86, B3LYP, CAM-B3LYP, X3LYP, B972, PBE0[PBE1PBE]). Additionally, series of aromatic compounds (C₆H₅CN, C₆H₅NH₂, C₆H₅NO₂, p-NO₂C₆H₄NH₂) have been also investigated using the same DFT functionals.

All calculations have been carried out for the reference geometry, optimized at the same level of theory with the Gaussian 09 software.^[47] The wavelengths corresponding to experimental measurements have been used for calculations of hyperpolarizability.

As could be seen from Table 1, the smallest, among proposed here STO^{##}(IIS)-3G_{el} basis set provides good correspondence of calculated and experimental data for HF and CO molecules, but remarkable overestimates dynamic hyperpolarizability for H₂O and underestimates analogous property for CH₃F, CH₃CN, and NO species. Calculated value of dynamic hyperpolarizability for NH₃ molecule is quite sensitive on



Table 1. Calculated and observed absol equation β expt = A β calc + B.	ute values of t	he first dynan	nic hyperpola	arizability (β, a.u.) a	at 694.3 nm a	and paramete	ers of the line	ar regression
Basis set	B3PW91	B3P86	B3LYP	CAM-B3LYP	X3LYP	PBE0	B972	Expt.
HF								
STO ^{##} (IIS)-3G _{el} (36) ^[a]	10.95	10.20	11.73	10.42	11.97	10.28	10.60	$10.9 \pm 1.0^{[b]}$
STO ^{##} (IIS)-3G _{el} /STO ^{##} (II)-3G _{el} (51)	11.52	12.03	12.83	11.48	12.79	11.43	11.67	
STO ^{##} (II)-3G _{el} / STO ^{##} (IIS)-3G _{el} (72)	8.81	8.10	9.37	8.16	9.41	8.36	8.76	
STO ^{##} (II)-3G _{el} (87)	8.21	7.67	8.46	7.54	8.60	7.82	8.03	
d-aug-cc-pVTZ (94)	8.37	8.40	8.35	7.45	8.15	8.17	7.96	
LPOL-FS(73)	8.89	9.06	9.00	8.07	8.79	8.46	8.54	
LPOL-FL(98)	8.50	8.72	8.55	7.67	8.33	8.06	8.13	
H ₂ O								
STO ^{##} (IIS)-3G _{el} (43)	29.41	27.98	31.57	26.04	31.36	7.27	27.85	$22.0 \pm 0.9^{[c]}$
STO ^{##} (IIS)-3G _{el} /STO ^{##} (II)-3G _{el} (73)	27.08	26.27	28.20	23.52	28.97	25.21	26.04	
STO ^{##} (II)-3G _{el} / STO ^{##} (IIS)-3G _{el} (79)	22.19	20.25	24.28	19.80	24.72	21.61	22.10	
STO ^{##} (II)-3G _{el} (109)	25.41	23.00	24.77	20.12	25.44	21.23	21.97	
d-aug-cc-pVTZ (126)	20.83	21.05	21.29	17.57	20.79	20.16	19.73	
LPOL-FS(96)	21.45	22.08	22.12	18.40	21.47	20.17	20.43	
LPOL-FL (130)	21.47	21.61	23.11	18.41	22.10	20.25	20.66	
NH ₃								
STO ^{##} (IIS)-3G _{el} (50)	44.2	41.05	48.95	32.70	49.3	40.38	43.02	48.9 ± 1.2 ^[c]
STO ^{##} (IIS)-3G _{el} /STO ^{##} (II)-3G _{el} (95)	43.75	39.68	47.91	29.41	49.32	39.6	42.65	
STO ^{##} (II)-3G _{el} / STO ^{##} (IIS)-3G _{el} (86)	51.07	47.84	59.01	38.94	60.02	47.89	50.72	
STO ^{##} (II)-3G _{el} (131)	52.05	47.18	56.75	36.83	57.34	48.52	51.83	
d-aug-cc-pVTZ (158)	44.65	44.93	48.32	32.85	47.03	43.23	42.05	
LPOL-FS(119)	44.58	45.11	49.18	32.98	47.12	41.78	42.94	
LPOL-FL(162)	44.81	44.78	48.51	33.25	47.76	42.40	44.20	
СО								
STO ^{##} (IIS)-3G _{el} (58)	33.22	33.48	32.93	31.55	32.59	32.38	32.67	29.9 ± 3.2 ^[c]
STO ^{##} (II)-3G _{el} (130)	32.91	33.57	32.7	31.17	32.43	32.26	32.59	
d-aug-cc-pVTZ (124)	31.64	32.53	30.92	29.32	30.54	30.56	30.42	
LPOL-FS(100)	30.01	28.91	27.81	25.67	27.56	27.92	31.67	
LPOL-FL(132)	31.50	31.66	30.79	29.20	30.63	30.46	30.96	
CH₃F								
STO ^{##} (IIS)-3G _{el} (79)	48.98	49.02	49.55	44.26	49.60	47.90	48.35	57.0 ± 4.2 ^[d]
STO ^{##} (IIS)-3G _{el} /STO ^{##} (II)-3G _{el} (124)	65.48	64.20	65.20	56.70	64.97	63.35	63.87	
STO ^{##} (II)-3G _{el} / STO ^{##} (IIS)-3G _{el} (159)	59.32	59.22	60.20	52.02	59.74	60.97	58.80	
STO ^{##} (II)-3G _{el} (196)	59.17	62.00	63.02	54.57	62.90	60.96	61.31	
d-aug-cc-pVTZ (220)	55.68	56.26	55.44	48.50	54.60	54.53	54.64	
LPOL-FS(169)	58.11	57.64	57.40	50.30	57.35	56.85	57.27	
LPOL-FL(228)	55.51	55.41	55.13	48.24	54.83	54.40	54.62	
CH ₃ CN								
STO ^{##} (IIS)-3G _{el} (108)	11.43	14.65	11.33	15.78	10.29	10.9	10.48	17.9 ± 1.1 ^[e]
STO ^{##} (II)-3G _{el} / STO ^{##} (IIS)-3G _{el} (216)	14.18	16.5	15.88	19.4	15.61	15.19	15.34	(1064nm)
STO ^{##} (II)-3G _{el} (261)	10.45	12.66	10.75	15.75	10.34	10.66	10.27	
d-aug-cc-pVTZ (282)	16.43	16.62	17.34	16.73	16.7	14.97	15.62	
LPOL-FS(219)	9.23	10.78	9.12	14.86	8.28	7.72	6.96	
LPOL-FL(294)	16.19	17.12	17.3	20.06	16.91	15.18	15.58	
NO								-
STO ^{##} (IIS)-3G _{el} (58)	24.96	24.40	24.50	22.32	24.30	24.88	24.55	$34.3 \pm 3.9^{[t]}$
STO ^{##} (II)-3G _{el} (130)	35.55	34.51	34.65	29.80	34.08	35.51	33.22	
d-aug-cc-pVTZ (124)	40.01	37.90	40.03	33.74	39.96	39.18	40.64	
LPOL-FS(100)	36.48	35.32	36.13	30.93	35.67	35.68	35.09	
LPOL-FL(132)	38.14	36.65	37.81	31.99	37.34	37.17	37.26	
STO ^{##} (IIS)-3G _{el}								
A	0.82	0.78	0.86	0.61	0.87	0.9	0.82	
В	3.16	4.16	3.07	6.75	2.55	-3.66	2.39	
R	0.927	0.936	0.912	0.904	0.91	0.938	0.932	
STO ^{**} (IIS)-3G _{el} /STO ^{**} (II)-3G _{el}								
A	1.03	0.96	1.03	0.78	1.04	0.97	1.00	
В	1.36	2.1	2.76	3.28	3.09	1.26	1.48	
R	0.967	0.947	0.984	0.887	0.987	0.953	0.968	
STO ^{**} (II)-3G _{el} / STO ^{**} (IIS)-3G _{el}								
A	1.11	1.08	1.18	0.85	1.18	1.11	1.09	
B	-3.8	-3.44	-3.22	1.00	-3.16	-3.88	-3.14	
К	0.998	0.999	0.991	0.986	0.988	0.997	0.999	



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TABLE 1. Continued								
Basis set	B3PW91	B3P86	B3LYP	CAM-B3LYP	X3LYP	PBE0	B972	Expt.
STO ^{##} (II)-3G _{el}								
A	1.14	1.13	1.24	0.90	1.25	1.16	1.19	
В	-4.01	-4.23	-6.27	-0.38	-6.31	-5.56	-6.25	
R	0.985	0.988	0.989	0.97	0.987	0.991	0.991	
d-aug-cc-pVTZ								
A	0.99	1.00	1.02	0.78	1.00	0.98	0.97	
В	-0.26	-0.38	-0.48	1.98	-0.56	-0.78	-0.48	
R	0.981	0.987	0.988	0.949	0.985	0.98	0.971	
LPOL-FL								
Α	0.99	0.97	1.00	0.74	1.00	0.96	0.98	
В	-0.25	0.22	0.04	3.54	-0.39	-0.73	-0.71	
R	0.987	0.991	0.993	0.950	0.993	0.984	0.988	
LPOL-FS								
A	1.07	1.05	1.11	0.81	1.1	1.05	1.07	
В	-4.09	-3.41	-4.89	0.30	-5.24	-4.83	-4.77	
R	0.981	0.988	0.987	0.968	0.985	0.975	0.972	
[a] Number of basis function is given in [50]. [e] SHG measured from Ref. [51]. [f]	parentheses. [SHG measured	b] SHG mea from Ref. [5	sured from R	ef. [48]. [c] SHG r	neasured fro	m Ref. [49]. [d] SHG measu	red from Ref.

functional used—one can see good correspondence for B3LYP and X3LYP approaches and underestimation for the rest of selected here functionals. LPOL basis sets have better correlation with the experimental data than d-aug-cc and practically coincide with STO##(II)-3G_{el} / STO##(IIS)-3G_{el}, but they are larger than our proposed basis sets.

Interestingly, augmentation of aforementioned basis set by additional d-orbitals for hydrogen atoms (STO^{##}(IIS)-3G_{el} / STO^{##}(II)-3G_{el} basis set) does affect the calculated values for HF and NH₃ molecules. Nevertheless, it remarkable decreases theoretical values for H₂O and increases predicted data for molecules containing methyl group (CH₃F and CH₃CN). These results are in better agreement of calculated and experimental data. For some reason, the calculation of hyperpolarizability using LPOL-FS basis set for CH3CN is significantly different from the experimental data that requires further consideration.

Much more pronounced improvement of accuracy could be obtained by adding d and f functions to non-hydrogen atoms $({\rm STO}^{\#}({\rm II}){\rm -3G}_{\rm el}/{\rm STO}^{\#}({\rm IIS}){\rm -3G}_{\rm el}$ basis set). As could be seen from Table 1, for all functional used here, except CAM-B3LYP, the correlation coefficients between experimental and calculated, using ${\rm STO}^{\#}({\rm II}){\rm -3G}_{\rm el}/{\rm STO}^{\#}({\rm IIS}){\rm -3G}_{\rm el}$ basis set, dynamic hyperpolarizability values are higher, or close to 0.99. Deviation of slope values from unity for those linear regressions is as small as 0.18, and intercept values do not exceed 3.5 a.u.

Further expansion of STO^{##}(II)-3G_{el} / STO^{##}(IIS)-3G_{el} basis set by addition of d-orbitals for hydrogen atoms, which results in STO^{##}(II)-3G_{el} basis set, does not lead to improvement of accuracy; even slightly worsening agreement of experimental and calculated values for the test set of molecules is noticed.

As could be seen from the analysis of correlation coefficients values (Table 1, 2) proposed here $\text{STO}^{\#}(\text{II})$ - $3G_{el} / \text{STO}^{\#}(\text{IIS})$ - $3G_{el}$ basis set shows better overall performance, if compare to the rest basis sets used. It also includes comparison with the recommended for calculations of dynamic hyperpolarizability d-aug-cc-pVTZ and LPOL-FL basis sets which is more than 20%

			$p-NO_2C_6H_4NH_2$	C_6H_5CN	$C_6H_5NH_2$				
Method	STO ^{##} (IIS)-3G _{el} (296) ^[a]	STO ^{##} (II)-3G _{el} / STO ^{##} (IIS)-3G _{el} (620)	LPOL-FL (754)	LPOL-FS (565)	aug-cc-pvtz (529)	d-aug-cc-pvtz (718)	STO ^{##} (IIS)-3G _{el} (332)	STO ^{##} (IIS)-3G _{el} (267)	STO ^{##} (IIS)-3G _{el} (252)
B3PW91	220.1	207.4	199.54	208.25	192.08	254.50	1128.79	39.62	170.1
B3P86	223.9	207.6	172.49	209.33	187.99	193.51	1153.91	37.64	169.2
B3LYP	240.0	229.7	219.70	232.33	211.595	217.54	1198.60	44.65	172.4
CAM-B3LYP	178.9	165.2	156.27	169.27	149.58	153.45	1007.23	22.00	172.6
X3LYP	229.2	222.0	213.32	224.62	205.34	211.85	1177.76	47.22	175.4
PBE0	196.4	187.1	178.80	185.14	171.82	175.92	1076.23	41.10	170.5
B972	206.8	197.4	189.80	197.55	184.21	187.70	1102.14	43.22	171.4
Expt.			1072 (1064 nm) ^[c]	41.7 (1910 nm) ^[d]	182.9 (1318 nm) ^[e]				



larger than STO^{##}(II)-3G_{el} / STO^{##}(IIS)-3G_{el} basis set. In contrast to the set of small molecules, collected in Table 1, for nitrobenzene, an aromatic molecule, the STO^{##}(IIS)-3G_{el} and STO^{##}(II)-3G_{el} / STO^{##}(IIS)-3G_{el} basis sets give rather close results (deviation does not exceed 10%). They are in better agreement with experimental value, if compare to the results obtained using LPOL-n, aug-cc-pVTZ, and d-aug-cc-pVTZ basis sets. Thus that small-sized STO^{##}(II)-3G_{el} basis set could be considered as accurate and cost effective choice for calculations of dynamic hyperpolarizability of aromatic compounds. This conclusion is supported by the results of calculations performed for three additional, aromatic compounds, as is illustrated by data collected in Table 2.

Conclusions

An augmentation of Slater-type basis sets by second-order correction functions is proposed here. The correction functions are obtained from the solution of the nonhomogeneous Schrödinger equation for the model problem "one-electron atom in an external uniform electric field," using the closed representation of the Green's function. Such approach allows for construction of physically adapted basis sets $\text{STO}^{\#}(\text{IIS})$ -3G_{el}. Novel basis sets, in combination with DFT approach, provide a useful, efficient tool for the theoretical study of dynamic hyperpolarizability.

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Keywords: Slater-type basis set • hyperpolarizability • DFT

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- Additional Supporting Information may be found in the online version of this article.
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