

# Novel Physically Adapted $\text{STO}^{\#\#}$ -3G Basis Sets. Efficiency for Prediction of Second-Order Electric and Magnetic Properties of Aromatic Hydrocarbons

E. Voronkov,<sup>[a]</sup> V. Rossikhin,<sup>\*,[b]</sup> S. Okovytyy,<sup>[c]</sup> A. Shatckih,<sup>[c]</sup> V. Bolshakov,<sup>[b]</sup> and J. Leszczynski<sup>[d]</sup>

Efficient scheme for construction of physically justified  $\text{STO}^{\#\#}$ -3G<sub>el</sub> and  $\text{STO}^{\#\#}$ -3G<sub>mag</sub> basis sets has been proposed. It is based upon the analysis of analytical form of the first-order correction functions to unperturbed STO basis sets under the perturbation by electric or magnetic fields. The test calculations of polarizability, magnetic susceptibility and chemical shifts performed for a series of aromatic compounds

within the developed basis set in the framework of Hartree-Fock and Density Functional Theory (DFT) approaches show good agreement of the predicted properties with experiments.  
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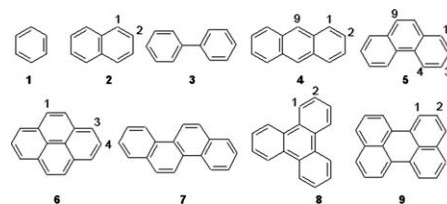
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## Introduction

Development of physically adapted basis sets of atomic orbitals (AO) for calculations of electric and magnetic properties of many-particle systems is still a challenging task for theoretical chemists, comparable in importance with improvement of quantum-chemical approaches. In our recent papers,<sup>[1,2]</sup> we have proposed a scheme for augmentation of basis sets, which is based upon the expansion of the first-order correction functions obtained applying perturbation theory for AO, on the unperturbed basis functions. Such corrections can be found either by the direct differentiating of unperturbed AO with respect to the perturbation parameter (see, for e.g., Ref. [3]) if AO explicitly depend on that parameter or by using the perturbation theory in the case of their implicit dependence.

It is well known<sup>[4]</sup> that the dependence of basic functions on the external magnetic field strength can be explicitly introduced by using of the so-called gauge-invariant AO. A similar procedure is also used for the determination of the molecular electric properties (see, e.g., Ref. [5]). Using the perturbation theory especially in the cases when it can be represented in the closed analytical form for the correction determination by Greens' function method is more straightforward and justified from both the mathematical and physical points of view. These approaches provide foundations to decrease the influence of effects caused by the limitation of the unperturbed AO basis set size in the calculation of such properties for which the knowledge of excited states is necessary: the polarizability, magnetic susceptibility, nuclear magnetic shielding tensor, and so on. It is necessary to note that in our previous paper<sup>[6]</sup> the procedure of expansion of an initial basis set of Gaussian-type orbital's (GTO) mentioned above is shown in details. However, in comparison with the GTO, choice of Slater-type orbital's (STO) is physically more justified for molecules as the exact wave function behaves in infinity following the same exponential dependence.

In this article, we propose an approach for physically justified extension of standard STO-3G basis set by functions obtained from STO analytical correction functions calculated by Green's function with correspondence to the property perturbation operator. The performance of such developed basis set for calculation of polarizability, magnetic susceptibility, and nuclear magnetic shielding tensor has been tested for the series of aromatic molecules: benzene (1), naphthalene (2), biphenyl (3), anthracene (4), phenanthrene (5), pyrene (6), chrysene (7), triphenylene (8), perylene (9), benzantracene (10), nitrobenzene (11), pyrrole (12), and furan (13).



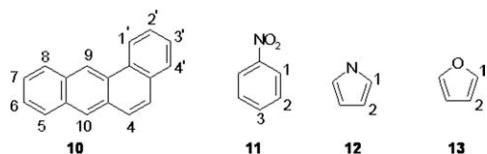
[a] E. Voronkov  
Dnepropetrovsk National University of Railway Transport, Dnepropetrovsk, Ukraine

[b] V. Rossikhin, V. Bolshakov  
Pridneprov's'ka State Academy of Civil Engineering and Architecture, Dnepropetrovsk, Ukraine  
E-mail: vvr375@gmail.com

[c] S. Okovytyy, A. Shatckih  
Dnepropetrovsk National University, named after Oles Gonchar, Dnepropetrovsk, Ukraine

[d] J. Leszczynski  
Jackson State University, Jackson, Mississippi

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## Theory

It is well known that STO functions, where functions decayed exponentially with distance from the nuclei, provide more accurate description of wave function if compare with GTO. However, considering significant computational difficulties for calculation of three- and four-center two-electron integrals, Slater functions are primarily used for atomic and diatomic system, or they are expanded in series of Gaussian-type orbitals which gives well-known STO-nG basis sets.

Determination of first-order correction function  $\chi^{(1)}$  to STO orbitals  $\chi^{(0)}$  is based on solution of nonhomogeneous Schrodinger equation

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

where  $V(r)$  is a potential that defines the type of basis set AO and  $\hat{W}(r)$  represents the perturbation operator.

From the solution of [Eq. (1)], it follows that the first-order correction to the solution  $\chi^{(0)}(r)$  corresponding to the homogeneous form ( $\lambda \hat{W}(r) \equiv 0$ ) is determined by the relation

$$\chi^{(1)}(r) = \int G_E(r, r') \hat{W}(r') \chi^{(0)}(r') dr' \quad (2)$$

where  $G_E(r, r')$  is the Green's function of the homogeneous Schrodinger equation. For the spherically symmetrical potential  $V(r)$  the Green's function can be expressed in the form

$$G_E(r, r') = \sum_{l,m} g_l(r, r'; E) Y_{lm}(r_0) Y_{lm}^*(r'_0) \quad (3)$$

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

Using Green's function approach in Refs. [7,8], we have obtained the analytical expressions for the correction functions of first-order perturbation theory for basis STO's in electric field (perturbation operator  $\hat{W}_z(r) = -r \cos\theta$ )

$$\begin{aligned} 1S^{(0)} &= \frac{\xi_1^{-3/2}}{\sqrt{3}} e^{-\rho} \rho (2 + \rho) Y_{10} \\ 2S^{(1)} &= \frac{\xi_2^{-3/2}}{6\sqrt{2}} e^{-\rho/2} \rho (30 - \rho^2) Y_{10} \\ 2P_{x,y}^{(1)} &= \frac{\xi_2^{-3/2}}{2\sqrt{30}} e^{-\rho/2} \rho^2 (6 + \rho) \left\{ \begin{matrix} Y_{21}^c \\ Y_{21}^s \end{matrix} \right\} \\ 2P_z^{(1)} &= \frac{\xi_2^{-3/2}}{3\sqrt{2}} e^{-\rho/2} \left[ \left( \frac{\rho^3}{2} - 3\rho^2 - 3\rho + 6 \right) Y_{00} + \frac{1}{\sqrt{5}} (\rho^3 + 6\rho^2) Y_{20} \right] \end{aligned} \quad (4)$$

and in magnetic field, where perturbation operator  $\hat{W}_x = -\frac{eh}{2mc} [\mathbf{R} \times \nabla]_x = \frac{eh}{2mc} (R_z \frac{\partial}{\partial y} - R_y \frac{\partial}{\partial z})$ :

$$\begin{aligned} 1S^{(1)} &= \frac{N_1}{\sqrt{3}} \rho e^{-\rho} (R_z Y_{11}^s - R_y Y_{10}) \\ 2S^{(1)} &= \frac{N_2}{\sqrt{3}} \rho^2 e^{-\rho} (R_z Y_{11}^s - R_y Y_{10}) \\ 2P_x^{(1)} &= 2P_x^{(0)} [\vec{R} \times \vec{p}]_x \\ 2P_y^{(1)} &= 2P_y^{(0)} \{ [\vec{R} \times \vec{p}]_x + \frac{3}{2} R_z (1 - \rho) / \xi y \} \\ 2P_z^{(1)} &= 2P_z^{(0)} \{ [\vec{R} \times \vec{p}]_x + \frac{3}{2} R_y (1 - \rho) / \xi y \} \\ 3S^{(1)} &= \frac{9\sqrt{30}}{2} N_3 e^{-\rho} (2\rho^3 - 12\rho^2 + 15\rho) (R_z Y_{11}^s - R_y Y_{10}) \\ 3P_x^{(1)} &= \frac{27}{2} N_3 e^{-\rho} (7\rho^2 - 2\rho^3) (R_z Y_{22}^s - R_y Y_{21}^c) \\ 3P_y^{(1)} &= \frac{243}{8} N_3 e^{-\rho} \left\{ \frac{2\sqrt{15}}{3} \left( -\rho^3 - 19\rho^2 + \frac{123}{2}\rho - \frac{63}{2} \right) R_z Y_{00} \right. \\ &\quad \left. + \rho^2 (-2\rho + 7) \left[ \left( \frac{1}{\sqrt{3}} Y_{20} + Y_{22}^c \right) R_z + Y_{21}^s R_y \right] \right\} \\ 3P_z^{(1)} &= \frac{243}{8} N_3 e^{-\rho} \left\{ \rho^2 (7 - 2\rho) \left( R_z Y_{21}^s - \frac{2}{\sqrt{3}} R_y Y_{20} \right) \right. \\ &\quad \left. - \frac{2\sqrt{15}}{3} \left( -\rho^3 - 19\rho^2 + \frac{123}{2}\rho - \frac{63}{2} \right) R_z Y_{00} \right\} \end{aligned} \quad (5)$$

In [eqs. (4) and (5)]  $\rho = \xi_i r$ , and  $Y_{lm}^c$  are the real spherical functions. Expressions for other components could be obtained in the same way.

For accurate description of the properties of molecules under action of external electric or magnetic field one has to use extended basis sets augmented by polarization and diffuse functions, which could be retrieved from correction functions of first-order perturbation theory (response functions), generated by corresponding perturbation operator. As could be seen from the analytical form of first-order correction functions [eqs. (4) and (5)], one can represent those functions as linear combination of atomic STO of strictly defined type and quantity. Changes of principal quantum number therein require corresponding variation of scaling factors.

It should be noted that in contrast to response functions, obtained from London AO for magnetic field, Greens' function method allows to obtain general solution of nonhomogeneous Schrodinger equation thus improving the quality of wave function in those regions of the configuration space that give the dominant contribution to the molecular properties under consideration. The same procedure could be applied to unperturbed basis sets of any type. It is also important to underline that the proposed approach for determination of addition functions does not require any additional procedure for optimization of nonlinear parameters of basis functions, namely orbital exponents.

Applying here the described procedure the following linear combinations have been obtained.

For electric field:

$$\begin{aligned} 1s^{(1)}(\xi_1) &\rightarrow [2p(\xi_1 * 0.5)] + 3p(\xi_1 * 0.333) \\ 2s^{(1)}(\xi_2) &\rightarrow 4p(\xi_2 * 0.5) + [2p(\xi_2)] \\ 2p^{(1)}(\xi_2) &\rightarrow [1s(\xi_2 * 2.0) + 3s(\xi_2 * 0.67) + 3d(\xi_2 * 0.67)] \\ &\quad + 4d(\xi_2 * 0.5) + 4s(\xi_2 * 0.5) \end{aligned} \quad (6)$$

**Table 1.** Calculated, corrected and observed polarizabilities ( $\text{\AA}^3$ ) for aromatic compounds (1–9, 11) and parameters of the linear regression equation  $\alpha_{\text{expt}} = A\alpha_{\text{calc}} + B$ .

Compound	Methods/Basis	RHF	BP86	B3LYP	PBE0	Expt. <sup>[13–15]</sup>
<b>1</b>	STO-3G	4.75	5.10	5.04	4.90	10.32; 10.74
	6-311G(d,p)	8.45	9.05	8.80	8.74	
	STO <sup>##</sup> -3G <sub>el</sub>	9.92	10.59	10.29	10.15	
	STO <sup>##</sup> -3G <sub>el</sub> cor.	10.13	10.13	10.12	10.13	
<b>2</b>	STO-3G	8.80	10.01	9.77	9.48	16.50; 17.48
	6-311G(d,p)	14.82	16.30	15.76	15.62	
	STO <sup>##</sup> -3G <sub>el</sub>	16.97	18.53	17.93	17.66	
	STO <sup>##</sup> -3G <sub>el</sub> cor.	17.22	17.04	17.10	17.10	
<b>3</b>	STO-3G	10.55	12.19	11.77	11.40	20.15
	6-311G(d,p)	17.81	19.89	19.09	18.92	
	STO <sup>##</sup> -3G <sub>el</sub>	20.09	22.29	21.43	21.13	
	STO <sup>##</sup> -3G <sub>el</sub> cor.	20.36	20.32	20.29	20.33	
<b>4</b>	STO-3G	13.86	16.43	15.88	15.37	25.40
	6-311G(d,p)	22.54	25.38	24.40	24.13	
	STO <sup>##</sup> -3G <sub>el</sub>	25.36	28.33	27.26	26.80	
	STO <sup>##</sup> -3G <sub>el</sub> cor.	25.66	25.58	25.62	25.59	
<b>5</b>	STO-3G	13.04	15.45	15.14	14.42	24.70
	6-311G(d,p)	21.33	24.04	23.09	22.85	
	STO <sup>##</sup> -3G <sub>el</sub>	24.15	26.98	25.90	25.50	
	STO <sup>##</sup> -3G <sub>el</sub> cor.	24.44	24.40	24.37	24.39	
<b>6</b>	STO-3G	15.67	18.45	17.84	17.29	28.22
	6-311G(d,p)	24.89	27.89	26.86	26.59	
	STO <sup>##</sup> -3G <sub>el</sub>	27.91	31.03	29.89	29.38	
	STO <sup>##</sup> -3G <sub>el</sub> cor.	28.23	27.93	28.02	27.99	
<b>7</b>	STO-3G	17.71	21.83	20.85	20.12	33.06
	6-311G(d,p)	28.53	32.89	31.41	31.02	
	STO <sup>##</sup> -3G <sub>el</sub>	32.04	36.45	34.88	34.29	
	STO <sup>##</sup> -3G <sub>el</sub> cor.	32.38	32.65	32.57	32.55	
<b>8</b>	STO-3G	18.31	20.57	19.73	19.06	31.07
	6-311G(d,p)	27.48	31.30	29.96	29.61	
	STO <sup>##</sup> -3G <sub>el</sub>	30.96	34.85	33.42	32.87	
	STO <sup>##</sup> -3G <sub>el</sub> cor.	31.29	31.26	31.24	31.23	
<b>9</b>	STO-3G	20.16	24.89	23.76	22.97	35.80
	6-311G(d,p)	31.87	36.72	35.09	34.66	
	STO <sup>##</sup> -3G <sub>el</sub>	35.53	40.45	38.72	38.06	
	STO <sup>##</sup> -3G <sub>el</sub> cor.	35.89	36.13	36.08	36.05	
<b>11</b>	STO-3G	6.46	7.17	6.96	6.74	12.92; 14.70
	6-311G(d,p)	10.36	11.58	11.14	11.00	
	STO <sup>##</sup> -3G <sub>el</sub>	12.23	13.68	13.15	12.90	
	STO <sup>##</sup> -3G <sub>el</sub> cor.	12.45	12.82	12.73	12.68	
<b>R</b>	STO-3G	0.9960	0.9988	0.9990	0.9987	
	6-311G(d,p)	0.9986	0.9992	0.9991	0.9991	
	STO <sup>##</sup> -3G <sub>el</sub>	0.9989	0.9993	0.9993	0.9992	
<b>A</b>	STO-3G	1.653	1.326	1.399	1.450	
	6-311G(d,p)	1.101	0.938	0.986	0.999	
	STO <sup>##</sup> -3G <sub>el</sub>	1.006	0.871	0.913	0.929	
<b>B</b>	STO-3G	2.434	3.645	3.285	3.257	
	6-311G(d,p)	0.908	1.766	1.571	1.516	
	STO <sup>##</sup> -3G <sub>el</sub>	0.149	0.903	0.728	0.697	
<b>MSE</b>	STO-3G	0.818	0.454	0.413	0.464	
	6-311G(d,p)	0.480	0.371	0.386	0.396	
	STO <sup>##</sup> -3G <sub>el</sub>	0.429	0.333	0.352	0.358	

For magnetic field:

$$\begin{aligned}
 1s^{(1)}(\xi_1) &\rightarrow 2p^{(0)}(\xi_1 * 0.5) \\
 2s^{(1)}(\xi_2) &\rightarrow 3p^{(0)}(\xi_2 * 0.67), \\
 2p^{(1)}(\xi_2) &\rightarrow 3d^{(0)}(\xi_2 * 0.67) + 3s^{(0)}(\xi_2 * 0.67) + [1s^{(0)}(\xi_2 * 2.0)], \\
 3s^{(1)}(\xi_3) &\rightarrow [2p^{(0)} + 3p^{(0)}] + 4p^{(0)}(\xi_3 * 0.75), \\
 3p^{(1)}(\xi_3) &\rightarrow 4d^{(0)}(\xi_3 * 0.75) + 4s^{(0)}(\xi_3 * 0.75) \\
 &\quad + [2s^{(0)}(\xi_3 * 1.5) + 1s^{(0)}(\xi_3 * 3.0)],
 \end{aligned}
 \tag{7}$$

Since radial parts of Slater orbitals contain just radius-vectors  $r$  with high order of magnitudes, the only terms with maximal principal quantum number from [Eqs. (6) and (7)] have been kept, and the terms quoted in square brackets are disregarded. By adding remained orbitals to the initial STO basis set, the following adapted STOs have been obtained for electric field

$$\{1s(\xi_1), 2s(\xi_2), 2p(\xi_2), 3p(\xi_1 * 0.333), 4s(\xi_2 * 0.5), 4p(\xi_2 * 0.5), 4d(\xi_2 * 0.5)\}
 \tag{8}$$

**Table 2.** Calculated, corrected, and observe diamagnetic susceptibilities (cgs-ppm/mol) of aromatic compounds (1–9, 11) and parameters of the linear regression equation  $\chi_{\text{expt}} = A\chi_{\text{calc}} + B$ . Sign is reversed.

Compound	Methods/Basis	HF	BP86	B3LYP	PBE0	Expt. <sup>[13,16]</sup>
<b>1</b>	STO-3G	62.60	58.83	59.39	59.85	55.00
	6-311G(d,p)	60.43	55.78	56.45	56.66	
	STO <sup>##</sup> -3G <sub>mag</sub>	60.07	55.57	56.20	56.47	
	STO <sup>##</sup> -3G <sub>mag</sub> cor.	53.89	54.06	54.00	53.86	
<b>2</b>	STO-3G	106.0	101.3	102.0	102.9	91.60
	6-311G(d,p)	101.14	94.87	95.72	96.16	
	STO <sup>##</sup> -3G <sub>mag</sub>	100.70	94.58	95.36	95.93	
	STO <sup>##</sup> -3G <sub>mag</sub> cor.	92.20	93.34	93.08	92.92	
<b>3</b>	STO-3G	120.50	112.44	113.74	114.70	103.3
	6-311G(d,p)	114.60	105.35	106.73	107.26	
	STO <sup>##</sup> -3G <sub>mag</sub>	114.33	104.87	106.20	106.97	
	STO <sup>##</sup> -3G <sub>mag</sub> cor.	105.06	103.70	103.90	103.85	
<b>4</b>	STO-3G	149.83	144.94	145.60	146.80	130.3
	6-311G(d,p)	141.57	134.48	135.43	136.04	
	STO <sup>##</sup> -3G <sub>mag</sub>	141.12	134.00	134.82	135.71	
	STO <sup>##</sup> -3G <sub>mag</sub> cor.	130.32	133.05	132.44	132.31	
<b>5</b>	STO-3G	148.10	141.28	142.16	143.37	127.9
	6-311G(d,p)	138.79	130.26	131.38	132.08	
	STO <sup>##</sup> -3G <sub>mag</sub>	138.57	130.02	131.09	131.96	
	STO <sup>##</sup> -3G <sub>mag</sub> cor.	127.91	129.03	128.74	128.59	
<b>6</b>	STO-3G	178.04	171.59	172.58	174.08	155.0
	6-311G(d,p)	166.44	158.02	159.29	160.05	
	STO <sup>##</sup> -3G <sub>mag</sub>	166.43	157.74	158.55	159.95	
	STO <sup>##</sup> -3G <sub>mag</sub> cor.	154.19	156.94	156.14	156.30	
<b>7</b>	STO-3G	191.92	183.41	184.60	186.23	167.0
	6-311G(d,p)	178.64	167.76	169.22	170.22	
	STO <sup>##</sup> -3G <sub>mag</sub>	178.71	167.7	168.99	170.35	
	STO <sup>##</sup> -3G <sub>mag</sub> cor.	165.77	166.97	166.56	166.60	
<b>8</b>	STO-3G	190.20	177.18	178.64	180.29	156.6
	6-311G(d,p)	172.56	160.32	162.04	163.13	
	STO <sup>##</sup> -3G <sub>mag</sub>	172.57	160.52	162.07	163.42	
	STO <sup>##</sup> -3G <sub>mag</sub> cor.	159.98	159.74	159.65	159.74	
<b>9</b>	STO-3G	202.30	186.87	190.30	192.23	167.5
	6-311G(d,p)	179.89	160.16	164.25	165.64	
	STO <sup>##</sup> -3G <sub>mag</sub>	178.30	159.48	163.11	164.52	
	STO <sup>##</sup> -3G <sub>mag</sub> cor.	165.38	158.70	160.69	160.83	
<b>11</b>	STO-3G	57.56	56.42	55.74	57.02	61.9
	6-311G(d,p)	68.66	62.44	63.31	64.02	
	STO <sup>##</sup> -3G <sub>mag</sub>	68.25	61.89	62.78	63.64	
	STO <sup>##</sup> -3G <sub>mag</sub> cor.	61.60	60.42	60.56	60.96	
<b>R</b>	STO-3G	0.996	0.9979	0.9975	0.9977	
	6-311G(d,p)	0.9994	0.9969	0.9982	0.9984	
	STO <sup>##</sup> -3G <sub>mag</sub>	0.9993	0.9967	0.9979	0.9980	
<b>A</b>	STO-3G	0.793	0.849	0.837	0.831	
	6-311G(d,p)	0.943	1.009	0.997	0.991	
	STO <sup>##</sup> -3G <sub>mag</sub>	0.943	1.007	0.998	0.990	
<b>B</b>	STO-3G	−10.090	−8.274	−9.090	−8.789	
	6-311G(d,p)	3.074	2.459	2.440	2.427	
	STO <sup>##</sup> -3G <sub>mag</sub>	2.758	1.901	2.091	2.047	
<b>MSE</b>	STO-3G	4.158	2.885	3.171	3.017	
	6-311G(d,p)	1.527	3.484	2.688	2.532	
	STO <sup>##</sup> -3G <sub>mag</sub>	1.690	3.644	2.913	2.849	

and magnetic field

$$\{1s(\zeta_1), 2s(\zeta_2), 2p(\zeta_2), 2p(\zeta_1 * 0.5), \\ 3p(\zeta_2 * 0.67), 3s(\zeta_2 * 0.67), 3d(\zeta_2 * 0.67)\}. \quad (9)$$

Using tabulated values of STO-3G expansions on Gaussian-type orbitals<sup>[9–11]</sup> STO<sup>##</sup>-3G<sub>el</sub> and STO<sup>##</sup>-3G<sub>mag</sub> basis sets have been constructed with orbital exponents obtained from [Eqs. (8) and (9)] correspondingly. Renormalization of additional Slater-type AO expanded in series of Gaussian-type functions has been done automatically using the Gaussian 09 package of program.<sup>[12]</sup>

## Results and Discussion

STO<sup>##</sup>-3G<sub>el</sub> and STO<sup>##</sup>-3G<sub>mag</sub> basis sets have been tested for calculations of second-order electric (polarizability), and magnetic properties (susceptibility and <sup>1</sup>H chemical shifts), correspondingly, for the series of aromatic compounds (**1–13**). <sup>1</sup>H Chemical shift calculations have been carried out in CCl<sub>4</sub> for compounds (**1–6**, **8–10**) and in CDCl<sub>3</sub> solution for compounds (**11–13**) using PCM UA0 model.

All calculations have been performed at Hartree-Fock and DFT levels (BP86, B3LYP, PBE0(PBE1PBE) functionals) using the

**Table 3.** Calculated, corrected and observed proton chemical shifts  $\delta_{\text{H}}$  (ppm) for aromatic compounds in  $\text{CCl}_4$  solution relative to TMS<sup>[a]</sup> (ppm) and parameters of the linear regression equation  $\delta_{\text{expt}} = A \cdot \delta_{\text{calc}} + B$ .

Compound	Proton	$\delta_{\text{H}}$ (GIAO)					$\delta_{\text{H}}$ cor. (GIAO)				Expt. <sup>[17–19]</sup>
		RHF	BP86		B3LYP	PBE0	RHF	BP86	B3LYP	PBE0	
			Our <sup>[b]</sup>	6-311G(d,p) <sup>[c]</sup>							
1	1	7.51	7.28	7.52	7.38	7.44	7.37	7.31	7.32	7.32	7.27
2	1	7.99	7.76	8.02	7.86	7.94	7.80	7.76	7.78	7.77	7.73
4	2	7.60	7.45	7.71	7.54	7.60	7.45	7.47	7.47	7.47	7.38
	1	8.10	7.96	8.26	8.04	8.13	7.90	7.95	7.95	7.94	7.93
	2	7.50	7.48	7.76	7.53	7.61	7.37	7.50	7.46	7.47	7.39
5	9	8.64	8.33	8.61	8.45	8.55	8.38	8.30	8.34	8.32	8.36
	1	8.03	7.79	8.06	7.89	7.97	7.83	7.79	7.80	7.80	7.80
	2	7.74	7.57	7.81	7.65	7.72	7.58	7.58	7.58	7.57	7.51
6	3	7.78	7.60	7.90	7.69	7.75	7.61	7.61	7.61	7.60	7.57
	4	8.81	8.62	9.03	8.70	8.81	8.53	8.58	8.57	8.56	8.62
	9	7.81	7.67	7.91	7.75	7.83	7.64	7.68	7.67	7.67	7.65
8	1	8.23	8.06	8.32	8.16	8.23	8.01	8.05	8.06	8.03	8.00
	3	8.38	8.15	8.41	8.27	8.35	8.14	8.13	8.16	8.14	8.10
	4	8.15	8.04	8.31	8.14	8.22	7.94	8.03	8.04	8.03	7.93
9	1	8.76	8.55	8.98	8.63	8.75	8.48	8.51	8.51	8.51	8.61
	2	7.77	7.56	7.84	7.64	7.73	7.60	7.57	7.57	7.58	7.58
10	1	8.34	7.97	8.41	8.09	8.21	8.11	7.96	7.99	8.02	8.11
	2	7.55	7.25	7.61	7.36	7.43	7.41	7.28	7.30	7.31	7.38
	3	7.79	7.39	7.66	7.52	7.61	7.62	7.41	7.45	7.47	7.57
11 <sup>[d]</sup>	1'	8.96	8.78	9.21	8.85	8.97	8.66	8.73	8.71	8.70	8.77
	2'	7.79	7.62	7.93	7.70	7.78	7.62	7.63	7.62	7.63	7.59
	3'	7.74	7.58	7.83	7.65	7.73	7.58	7.59	7.58	7.58	7.53
	4'	7.95	7.75	8.04	7.83	7.92	7.76	7.75	7.75	7.75	7.76
	3	7.62	7.59	7.85	7.64	7.73	7.47	7.60	7.57	7.58	7.55
	4	7.80	7.75	7.99	7.81	7.90	7.63	7.75	7.73	7.74	7.72
	5	8.15	8.00	8.28	8.07	8.16	7.94	7.99	7.97	7.97	8.03
12 <sup>[d]</sup>	6	7.64	7.58	7.85	7.63	7.71	7.49	7.59	7.56	7.56	7.47
	7	7.63	7.59	7.86	7.64	7.72	7.48	7.60	7.57	7.57	7.47
	8	8.25	8.06	8.39	8.14	8.24	8.03	8.05	8.04	8.04	8.03
	9	9.36	9.13	9.52	9.22	9.34	9.01	9.06	9.07	9.04	9.08
	10	8.52	8.28	8.53	8.38	8.47	8.27	8.26	8.27	8.25	8.28
	1	8.75	8.16	8.44	8.34	8.42	8.47	8.14	8.23	8.21	8.23
	2	7.72	7.56	7.78	7.65	7.71	7.56	7.57	7.58	7.56	7.56
13 <sup>[d]</sup>	3	8.13	7.77	7.94	7.89	7.95	7.92	7.77	7.80	7.78	7.71
	1	6.78	6.47	6.80	6.59	6.58	6.73	6.54	6.57	6.54	6.68
MSE	2	6.16	6.09	6.31	6.18	6.18	6.18	6.17	6.18	6.18	6.22
	1	7.25	7.21	7.64	7.28	7.24	7.14	7.24	7.22	7.14	7.47
R	2	6.36	6.35	6.60	6.43	6.43	6.35	6.42	6.42	6.41	6.35
A		0.9870	0.9898	0.9940	0.9916	0.9899					
B		0.886	0.950	0.911	0.949	0.904					
MSE		0.720	0.389	0.429	0.316	0.595					
		0.094	0.084	0.064	0.076	0.083					

[a] The calculated values of  $\sigma(^1\text{H})$  shielding constants in TMS are 32.29, 31.42, 31.80, and 31.67 for RHF, BP86, B3LYP, and PBE1PBE approaches, correspondingly. [b] STO<sup>##</sup>-3G<sub>mag</sub> basis set for C, N, O and STO-3G basis set for H atoms. [c] For TMS/BP86/6-311G(d,p) the value of  $\sigma(^1\text{H})$  is 31.58. [d] The values of  $\sigma(^1\text{H})$  for compounds (**11–13**) were obtained in  $\text{CDCl}_3$  solution. The values of  $\sigma(^1\text{H})$  for TMS are 32.29, 31.43, 31.81 and 31.68 for above-mentioned approaches, correspondingly.

reference geometries optimized at the same level of theory. Since STO<sup>##</sup>-3G<sub>el</sub> and STO<sup>##</sup>-3G<sub>mag</sub> basis sets have been obtained on base of AO Cartesian representation the “6d” keyword has been used for calculations. For calculations of molecular properties (polarizability and magnetic susceptibility) STO<sup>##</sup>-3G<sub>el</sub> and STO<sup>##</sup>-3G<sub>mag</sub> basis sets have been applied for whole set of nuclei while in the case of magnetic shielding calculations STO<sup>##</sup>-3G<sub>mag</sub> basis set has been applied for “heavy” nuclei and original STO-3G basis for nuclei of interest (protons). Such combination of basis sets is based on the property of first-order correction functions, which in the case of external magnetic field equals zero at the point of origin ( $R_{x,y,z} = 0$ ).

The calculated and experimental values of the properties of interest as well as parameters of the linear regression equation and obtained using those parameters are collected in Tables 1–3. For comparison, electric and magnetic properties, have been calculated with ‘parent’ standard STO-3G and triple-split Gaussian-type 6-311G(d,p) basis set (see Tables 1–3). It should be noted that the STO<sup>##</sup>-3G<sub>el</sub> and STO<sup>##</sup>-3G<sub>mag</sub> basis sets includes just 18 basis functions for C, N, O atoms and 4 basis functions for H atoms, which is more than in 10% less if compare with 6-311G(d,p) basis set. To remove systematic errors empirical corrections for the calculated values has been applied using linear scaling procedure (denoted as ‘cor.’) as proposed by Chesnut<sup>[20]</sup> and



performed recently in Refs. [21–28]. Such correction allows one to predict the ‘exact’ value of the corresponding property just performing calculations for the molecule of interest and applying obtained scaling factors (intercepts and slopes) from Tables 1–3.

As could be seen from Table 1, an application of the standard STO-3G leads to significant underestimation of polarizabilities. Deviation from experiment in absolute values increases for polyaromatic hydrocarbons (**4–9**) if compare with benzene (**1**), naphthalene (**2**) and biphenyl (**3**). This effect is more pronounced at Hartree-Fock level (up to  $17.49 \text{ \AA}^3$  for triphenylene (**8**) not taking into account electron correlation effects). An application of the BP86 functional gives slightly better agreement with experiment than the other, considered DFT functionals. Using of developed  $\text{STO}^{\#}\text{-3G}_{\text{el}}$  basis set significantly improves accuracy of calculations, for all theoretical approaches mean-square error does not exceed  $0.4 \text{ \AA}^3$ . Calculations using 6-311G(d,p) basis set results in better agreement with experiment if compare with standard STO-3G but MSE and intercept (B) values still larger than those obtained for  $\text{STO}^{\#}\text{-3G}_{\text{el}}$  basis set.

In contrast to polarizability, the values of magnetic susceptibility, calculated with STO-3G basis sets are significantly overestimated if compare with experimental data (see Table 2). Again, at HF and DFT levels the bigger aromatic molecule, the larger deviation is observed. The  $\text{STO}^{\#}\text{-3G}_{\text{mag}}$  basis sets yields much better agreement with experiment. Linear regression analyses show that the results calculated using adapted basis set have the slope closer to unity and smaller intercept if compare with values, calculated with STO-3G basis sets. Calculated using  $\text{STO}^{\#}\text{-3G}_{\text{mag}}$  basis set values are rather close to values calculated with triple-split 6-311G(d,p) with slight advantage of physically adapted basis set in intercept value at DFT level. Surprisingly, the results obtained at HF/ $\text{STO}^{\#}\text{-3G}_{\text{mag}}$  level of theory are slightly better than those calculated at DFT/ $\text{STO}^{\#}\text{-3G}_{\text{mag}}$  level.

The data in Table 3 clearly demonstrate an efficient performance of the proposed basis sets for calculations of nuclear magnetic shielding constants. Thus, deviation of absolute values of chemical shifts does not exceed 0.3 ppm and mean-square error is within 0.05–0.06 ppm. Linear regression equation for chemical shifts calculated at BP86/ $\text{STO}^{\#}\text{-3G}_{\text{mag}}$  level of theory characterized by smaller value of intercept and closer to unity slope if compare with calculation at BP86/6-311G(d,p) level.

## Conclusions


This article describes the method of construction of improved basis sets for calculations of second-order electric and magnetic properties based upon the (1) expansion analytical form of the first-order correction functions on STO; (2) augmentation of the initial STO basis set using obtained functions; and (3) expansion of the STO resulting functions in the terms of GTO basis set which could be done using any quantum-chemical package containing Gaussian-type orbitals. Good agreement with experimental data of the predicted values of polarizability, magnetic susceptibility, and chemical shifts calculated using cost-effective  $\text{STO}^{\#}\text{-3G}_{\text{el}}$  and  $\text{STO}^{\#}\text{-3G}_{\text{mag}}$  basis sets for the group of aromatic compounds confirms high efficiency of the constructed basis sets and applicability of the proposed approach for basis expansion.

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