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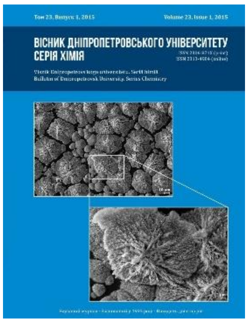

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NEW STO(II)-3G$_{\text{mag}}$ FAMILY BASIS SETS FOR THE CALCULATIONS OF THE MOLECULES MAGNETIC PROPERTIES

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Abstract

An efficient approach for construction of physically justified STO(II)-3Gmag family basis sets for calculation of molecules magnetic properties has been proposed. The procedure of construction based upon the taken into account the second order of perturbation theory in the magnetic field case. Analytical form of correction functions has been obtained using the closed representation of the Green functions by the solution of nonhomogeneous Schrödinger equation for the model problem of "one-electron atom in the external uniform magnetic field". Their performance has been evaluated for the DFT level calculations carried out with a number of functionals. The test calculations of magnetic susceptibility and 1H nuclear magnetic shielding tensors demonstrated a good agreement of the calculated values with the experimental data.

Key words: basis set; atomic orbitals; nuclear magnetic shielding tensors; magnetic susceptibility; DFT.

НОВЕ СІМЕЙСТВО БАЗИСІВ STO(II)-3G$_{\text{mag}}$ ДЛЯ РОЗРАХУНКІВ МАГНІТНИХ ВЛАСТИВОСТЕЙ МОЛЕКУЛ

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Анотація

Запропоновано ефективний спосіб побудови фізично адаптованих базисних наборів STO(II)-3G$_{\text{mag}}$ для розрахунків магнітних властивостей молекул. Спосіб побудови ґрунтується на врахуванні явних виразів для корекційних функцій другого порядку теорії збуджень по магнітному полю до базисних атомних орбіталей. Аналітичний вигляд корекційних функцій отримано шляхом застосування замкнутої форми функції Гріна у ході розв'язання неоднорідного рівняння Шредінгера для модельної задачі "одноелектронний атом у зовнішньому однорідному магнітному полі". Ефективність цих базисів продемонстровано на прикладі розрахунків магнітної сприйнятливості й тензорів магнітного екранування ядер ^{1}H для ряду молекул. Розрахунки здійснено в межах DFT із застосуванням різних функціоналів.

Ключові слова: базисний набір; атомні орбіталі; тензори ядерного магнітного екранування; магнітна сприйнятливість; теорія функціонала густини.

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НОВОЕ СЕМЕЙСТВО БАЗИСОВ STO(II)-3G$_{mag}$ ДЛЯ РАСЧЕТОВ МАГНИТНЫХ СВОЙСТВ МОЛЕКУЛ

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Аннотация

Предложен эффективный способ построения физически адаптированных базисных наборов STO(II)-3Gmag для расчета магнитных свойств молекул. Способ построения основан на учете явных выражений для поправочных функций второго порядка теории возмущений по магнитному полю к базисным атомным орбиталям. Аналитический вид поправочных функций получен путем использования замкнутого представления функции Грина при решении неоднородного уравнения Шредингера для модельной задачи "одноэлектронный атом во внешнем однородном магнитном поле". Эффективность этих базисов продемонстрирована в расчетах магнитной восприимчивости и тензоров магнитного экранирования ядер 1H для ряда молекул. Расчеты проведены в рамках DFT с применением различных функционалов.

Ключевые слова: базисный набор; атомные орбитали; тензоры ядерного магнитного экранирования; магнитная восприимчивость; теория функционала плотности. .

Introduction

The quantum-chemical calculations of the magnetic properties of molecules have become increasingly important owing to their contribute to the understanding the nature of chemical bonding and solution of some issues related with the structure and properties of molecular systems [1–2]. Various methods of calculations, such as theory of gauge-invariant atomic orbitals (GIAO) [3–4] and method of continuous gauge transformation (CSGT) [5], implemented in the framework of Hartree-Fock approximation (CHF) [6–8], density functional theory (DFT) [9] and others provide facilities for calculations of chemical compounds magnetic properties. For the exact calculations of magnetic properties it is necessary to use extended basis sets of atomic orbitals which can qualitatively describe the changes in the electron density of the molecule under external magnetic field for the obtaining of sufficiently accurate calculated values of the magnetic properties, such as nuclear magnetic shielding tensor (chemical shifts) and magnetic susceptibility.

For construction of the basis set corresponding to the requirements stated above, in most cases a simple "expansion" of the initial basis set of atomic orbitals (AO) by adding a new polarization and diffuse AOs have been used. However, the number of additional functions and their functional form at this case are not physically justified and based mostly on the erudition and some empirical rules. Among the existing basis sets for the calculations of the magnetic properties the sets of Dunning (aug-cc-pVXZ) [10–11] and Jensen (pc-n) [12–13] have become widely used.

Recently STO$^{\#\#}$-3G$_{el}$ and STO$^{\#\#}$-3G$_{mag}$ basis sets have been proposed for the calculation of electrical or magnetic properties of molecules [14], which have been constructed using the augmentation of STO-3G basis set by the first order correction functions of perturbation theory in electrical and magnetic fields case, respectively. As have been shown in [14–18], these basis sets demonstrate high efficiency which inspires us for their further improvement.

STO$^{\#\#}$(II)-3G$_{el}$ and STO$^{\#\#}$(IIS)-3G$_{el}$ basis sets, constructed based on the explicit expressions of the second order correction functions of the perturbation theory in the electric field, shown to be accurate and cost-effective for the calculations of the molecules polarizability and hyper-polarizability [19]. This paper is devoted to the further development of the approach proposed in [19] to construction of basis sets for calculation of magnetic properties based on the application of correction functions of the second-order perturbation theory in the magnetic field case. Analytical form of such correction functions has been obtained using the closed representation of the Green functions by the solution of nonhomogeneous Schrödinger equation for the model problem of "one-electron atom in the external uniform magnetic field" [20–21].

Theory

In [19] the method of augmentation of the original STO-3G basis set to STO$^{\#\#}$-3G$_{mag}$ basis set have been proposed by using the additional AOs contained in the analytical expressions of the first order correction function, which correspond to the angular momentum operator L as the perturbation operator. By consequential extension, we have taken into account the next (second) order of perturbation theory, where in the case of the magnetic field the corresponding operator is:

$$\hat{W}\,(r) = r^2 \sin^2 \theta. \qquad (1)$$

The second order correction functions has been obtained base on the solution of the nonhomogeneous Schrödinger equation:

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

Using a closed representation of the Green's function, it is possible to obtain an explicit analytical expression of correction functions, which are defined by the formula:

$$\chi^{(2)}(r) = \int G_E\,(r, r')\, \hat{W}(r')\, \chi^{(0)}(r')dr' \qquad (3)$$

where $G_E(r, r')$ – the Green's function, $V(r)$ – the operator of the potential energy that defines the type of orbitals, $\hat{W}(r')$ – the perturbation operator (1).

The analytical expressions for the second-order corrections to the hydrogen AOs have been obtained earlier by the authors [22], and transformed by us:

$$1S^{(2)} = \frac{4}{3} Y_{00}\, e^{-r} \left(\frac{11}{2} - r^2 - \frac{1}{3}r^3\right) + \frac{2}{3\sqrt{5}} Y_{20}\, e^{-r} \left(r^2 + \frac{2}{3}r^3\right)$$

$$2S^{(2)} = \frac{2}{3}\left(\frac{1}{\sqrt{2}} Y_{00}\, e^{-\frac{r}{2}} \left(328 - 164r - 14r^2 + \frac{7}{3}r^3 + \frac{1}{3}r^4\right) - \frac{1}{\sqrt{10}} Y_{20} e^{-\frac{r}{2}} \left(8r^2 + \frac{4}{3}r^3 - \frac{1}{3}r^4\right)\right)$$

$$2P_x^{(2)} = \frac{4}{5}\left(\frac{1}{2\sqrt{6}} Y_{11}^{c}\, e^{-\frac{r}{2}} \left(320r - 6r^3 - \frac{2}{3}r^4\right) + \frac{1}{3\sqrt{84}} Y_{31}^{c}\, e^{-\frac{r}{2}}\, (4r^3 + r^4)\right)$$

$$2P_y^{(2)} = \frac{4}{5}\left(\frac{1}{2\sqrt{6}} Y_{11}^{s}\, e^{-\frac{r}{2}} \left(320r - 6r^3 - \frac{2}{3}r^4\right) + \frac{1}{3\sqrt{84}} Y_{31}^{s} e^{-\frac{r}{2}}\, (4r^3 + r^4)\right)$$

$$2P_z^{(2)} = \frac{2}{5}\left(\frac{1}{2\sqrt{6}} Y_{10}\, e^{-\frac{r}{2}} \left(320r - 6r^3 - \frac{2}{3}r^4\right) + \frac{1}{\sqrt{126}} Y_{30}\, e^{-\frac{r}{2}}\, (4r^3 + r^4)\right)$$

$$3S^{(2)} = \frac{4}{9\sqrt{3}} Y_{00}\, e^{-\frac{r}{3}} \left(\frac{7371}{2} - 2457r + 204r^2 + 23r^3 - \frac{2}{3}r^4 - \frac{2}{27}r^5\right)$$
$$- \frac{2\sqrt{5}}{15\sqrt{3}} Y_{20} e^{-\frac{r}{3}} \left(112r^2 - \frac{2}{9}r^4 - \frac{4}{81}r^5\right)$$

$$3P_x^{(2)} = \frac{4}{5}\left(\frac{1}{\sqrt{6}} Y_{11}^{c}\, e^{-\frac{r}{3}} \left(1080r - 180r^2 - \frac{32}{2}r^3 + \frac{16}{27}r^4 + \frac{4}{81}r^5\right)\right.$$
$$\left. - \frac{2}{3\sqrt{84}} Y_{31}^{c}\, e^{-\frac{r}{3}} \left(4r^3 + \frac{1}{3}r^4 + \frac{2}{27}r^5\right)\right)$$

$$3P_y^{(2)} = \frac{4}{5}\left(\frac{1}{\sqrt{6}} Y_{11}^{s}\, e^{-\frac{r}{3}} \left(1080r - 180r^2 - \frac{32}{2}r^3 + \frac{16}{27}r^4 + \frac{4}{81}r^5\right)\right.$$
$$\left. - \frac{2}{3\sqrt{84}} Y_{31}^{s}\, e^{-\frac{r}{3}} \left(4r^3 + \frac{1}{3}r^4 + \frac{2}{27}r^5\right)\right)$$

$$3P_z^{(2)} = \tfrac{2}{5}\left(\tfrac{1}{\sqrt{6}} Y_{10}\, e^{-\frac{r}{3}} \left(1080r - 180r^2 - \tfrac{32}{2}r^3 + \tfrac{16}{27}r^4 + \tfrac{4}{81}r^5\right) - \tfrac{2}{\sqrt{126}} Y_{30} e^{-\frac{r}{3}} \left(4r^3 + \tfrac{1}{3}r^4 + \tfrac{2}{27}r^5\right)\right). \qquad (3)$$

were – the true spherical harmonics.

By using the rule of the selection new orbital exponents [15]:

$$\xi_{\mathrm{new}} = \frac{\mathrm{n_{old}} \cdot \xi_{\mathrm{old}}}{\mathrm{n}_{new}}, \qquad (4)$$

were ξ_{old} – the orbital exponent of the unperturbed AO,

$\mathrm{n_{old}}$ – the quantum number of the unperturbed AO,

$\mathrm{n_{new}}$ – the quantum number of the new AO,

from the expressions (3) one can generate the new Slater AOs with keeping only the expansion of new AOs with the higher quantum numbers $\mathrm{n_{new}}$:

$$1S^{(2)}(\xi_1) \rightarrow 3s\left(\xi_1 \cdot \tfrac{1}{3}\right), 4s\left(\xi_1 \cdot \tfrac{1}{4}\right), 3d\left(\xi_1 \cdot \tfrac{1}{3}\right), 4d(\xi_1 \cdot \tfrac{1}{4});$$
$$2S^{(2)}(\xi_2) \rightarrow 3s\left(\xi_2 \cdot \frac{2}{3}\right), 4s\left(\xi_2 \cdot \frac{1}{2}\right), 5s\left(\xi_2 \cdot \frac{2}{5}\right), 3d\left(\xi_2 \cdot \frac{2}{3}\right), 4d\left(\xi_2 \cdot \frac{1}{2}\right), 5d\left(\xi_2 \cdot \frac{2}{5}\right);$$
$$2P^{(2)}(\xi_2) \rightarrow 4p\left(\xi_2 \cdot \frac{1}{2}\right), 5p\left(\xi_2 \cdot \frac{2}{5}\right), 4f\left(\xi_2 \cdot \frac{1}{2}\right), 5f\left(\xi_2 \cdot \frac{2}{5}\right);$$
$$3S^{(2)}(\xi_3) \rightarrow 4s\left(\xi_3 \cdot \frac{3}{4}\right), 5s\left(\xi_3 \cdot \frac{3}{5}\right), 6s\left(\xi_3 \cdot \frac{1}{2}\right), 3d(\xi_3), 5d\left(\xi_3 \cdot \frac{3}{5}\right), 6d\left(\xi_3 \cdot \frac{1}{2}\right);$$
$$3P^{(2)}(\xi_3) \rightarrow 4p\left(\xi_3 \cdot \tfrac{3}{4}\right), 5p\left(\xi_{3 \cdot \frac{3}{5}}\right), 6p\left(\xi_3 \cdot \tfrac{1}{2}\right), 4f\left(\xi_3 \cdot \tfrac{3}{4}\right), 5f\left(\xi_3 \cdot \tfrac{3}{5}\right), 6f(\xi_3 \cdot \tfrac{1}{2}). \qquad (5)$$

Using all of additional functions from the right side of expression (5) as additional diffuse and polarization AOs (as in [19]), for the expansion of the original Slater-type basis set of atomic orbitals

$$1\mathrm{s}(\xi_1), 2\mathrm{s}(\xi_2), 2\mathrm{p}(\xi_2), 3\mathrm{s}(\xi_3), 3\mathrm{p}(\xi_3) \qquad (6)$$

with the following expansion by primitive Gaussian orbitals [23-25], leads to the construction of the new STO(IIF)-3G$_{\mathrm{mag}}$ basis set or its light versions – STO(IIM)-3G$_{\mathrm{mag}}$ and STO(IIV)-3G$_{\mathrm{mag}}$ basis sets, for which only functions with the same symmetry as the unperturbed occupied and valence AOs, or only the valence AOs as the additional AOs from (5) have been used. Symbols F, M, V means full, middle, and valence, respectively.

Results

Efficiency of constructed basis sets have been tested by calculations of the magnetic susceptibility for the number of molecules (some hydrocarbons, hydrides, CO, CO_2, CH_2O, N_2, F_2), carried out at HF method and DFT functionals B3LYP, BP86, PBE1PBE using the GAUSSIAN 09W program packages [26]. The results of these calculations are presented in the Table 1. Developed here basis sets have shown a good agreement with the experimental data. Furthermore, for such molecules as C_2H_2, CH_4, HCN, NH_3, SiH_4, and F_2 these basis sets have shown more acceptable results if compare to STO$^{\#\#}$-3G$_{mag}$, Jensen (pc -2, pcJ-2) and Dunning (aug-cc-pVTZ) basis sets. It is worth to note, that STO(IIM)-3G$_{mag}$ and STO(IIV)-3G$_{mag}$ basis sets give sufficiently accurate and in some cases even better results for the calculation of the magnetic susceptibility if compare to the STO(IIF)-3G$_{mag}$ basis set.

Table 1

Diamagnetic susceptibility of molecules χ (cgs-ppm/mol) (sign is reversed) and the parameters of the linear regression equation χ_{expt}=A* χ_{calc} + B

Method	STO(II*F*)-3G$_{mag}$	STO(IIM)-3G$_{mag}$	STO(IIV)-3G$_{mag}$	STO$^{\#\#}$-3G$_{mag}$	pc-2	pcJ-2	aug-cc-pVTZ	Experiment [27]
1	2	3	4	5	6	7	8	9
				C_2H_6				
HF	31.48	30.25	29.99	29.29	29.60	29.58	29.56	27.4
BP86	30.90	29.82	29.79	28.54	29.38	29.38	29.34	
B3LYP	30.41	29.72	29.64	28.63	29.27	29.26	29.23	
PBE1PBE	31.14	29.91	29.83	28.92	29.47	29.45	29.42	
				C_2H_4				
HF	19.46	21.54	21.35	21.02	21.30	21.30	21.30	19.7
BP86	17.83	20.22	20.16	19.65	20.03	20.03	20.00	
B3LYP	18.82	20.50	20.43	19.85	20.30	20.30	20.28	
PBE1PBE	18.40	20.48	20.42	19.84	20.21	20.21	20.20	
				C_2H_2				
HF	21.28	23.70	23.67	22.97	22.99	22.99	22.99	20.8
BP86	20.73	23.10	22.92	22.22	22.16	22.04	22.22	
B3LYP	21.39	23.41	23.24	22.38	22.35	22.35	22.40	
PBE1PBE	20.91	23.15	23.01	22.23	22.17	22.17	22.22	
				CH_4				
HF	18.19	18.32	18.33	19.1	18.96	18.87	18.88	17.4
BP86	18.59	18.99	18.97	19.52	19.29	19.27	19.27	
B3LYP	18.32	18.84	18.83	19.34	19.15	19.14	19.13	
PBE1PBE	18.46	18.90	18.89	19.43	19.24	19.22	19.22	
				HCN				
HF	17.70	17.42	17.51	16.53	17.05	17.04	17.03	16.8
BP86	16.64	16.47	16.48	15.33	15.97	15.98	16.00	
B3LYP	17.01	16.81	16.82	15.68	16.32	16.32	16.33	
PBE1PBE	16.80	16.62	16.65	15.56	16.12	16.12	16.13	
				CO				
HF	12.95	12.88	13.01	11.04	12.78	12.77	12.78	11.8
BP86	12.52	12.53	12.56	10.22	12.23	12.23	12.32	
B3LYP	12.76	12.74	12.79	10.53	12.49	12.49	12.56	
PBE1PBE	12.56	12.55	12.61	10.40	12.30	12.30	12.37	
				CO_2				
HF	23.73	23.03	23.17	22.68	22.49	22.46	22.45	21
BP86	22.94	22.46	22.46	21.95	21.90	21.89	21.86	
B3LYP	23.08	22.55	22.59	22.09	22.05	22.03	22.00	
PBE1PBE	23.10	22.53	22.58	22.08	21.99	21.97	21.95	
				CH_2O				
HF	8.02	8.44	8.49	8.19	8.53	8.54	8.54	6.86
BP86	6.10	6.56	6.54	6.27	6.58	6.59	6.59	
B3LYP	6.51	6.97	6.96	6.66	7.00	7.00	7.01	
PBE1PBE	6.52	6.9	6.90	6.59	6.91	6.91	6.89	
				H_2O				
HF	14.68	14.45	14.62	14.23	13.75	13.76	13.85	13.12
BP86	15.11	14.76	14.95	14.88	14.11	14.15	14.38	
B3LYP	15.03	14.69	14.87	14.76	14.05	14.04	14.29	
PBE1PBE	14.92	14.56	14.74	14.63	13.97	13.97	14.18	

Table 1 (continuing)

1		2	3	4	5	6	7	8	9
					NH_3				
HF		16.99	17.16	17.2	17.66	17.16	17.16	17.23	16.3
BP86		17.51	17.73	17.8	18.15	17.49	17.49	17.68	
B3LYP		17.45	17.59	17.65	18.03	17.41	17.4	17.58	
PBE1PBE		17.35	17.51	17.57	17.94	17.37	17.36	17.52	
					HF				
HF		10.47	10.54	10.58	10.51	10.33	10.41	10.38	10.4
BP86		10.99	11.06	11.08	11.20	10.67	10.67	10.84	
B3LYP		10.91	10.97	11.00	11.00	10.62	10.62	10.77	
PBE1PBE		10.82	10.88	10.91	10.90	10.55	10.55	10.68	
					SiH_4				
HF		21.47	23.87	22.86	21.35	21.73	21.92	21.99	20.4
BP86		22.85	25.10	23.89	22.30	23.22	23.35	23.52	
B3LYP		22.07	24.77	23.45	21.82	22.63	22.78	22.95	
PBE1PBE		22.69	25.03	23.88	22.20	22.99	23.16	23.32	
					H_2S				
HF		27.40	28.25	28.08	26.61	27.25	27.24	27.42	25.5
BP86		27.88	28.33	28.17	26.58	27.49	27.45	27.77	
B3LYP		27.80	28.26	28.10	26.50	27.37	27.34	27.64	
PBE1PBE		27.75	28.32	28.16	26.60	27.43	27.40	27.70	
					N_2				
HF		12.99	12.63	12.65	11.04	12.74	12.73	12.81	12
BP86		12.07	11.99	11.98	9.83	11.76	11.75	12.00	
B3LYP		12.32	12.24	12.23	10.18	12.11	12.10	12.33	
PBE1PBE		12.19	12.06	12.07	10.10	11.93	11.92	12.12	
					F_2				
HF		12.62	12.47	12.58	12.38	12.59	12.59	12.54	9.63
BP86		10.12	9.89	9.87	10.16	9.92	9.94	9.94	
B3LYP		10.81	10.63	10.63	10.71	10.64	10.65	10.64	
PBE1PBE		11.24	11.08	11.09	11.10	11.12	11.13	11.10	
HF	R	9	0.9912	0.9925	0.9871	0.9925	0.9927	0.9929	
	A	0.91	0.90	0.92	0.92	0.95	0.95	0.95	
	B	0.18	0.15	−0.18	0.30	−0.42	−0.43	−0.43	
BP86	R	0.9845	0.9893	0.9929	0.9821	0.9936	0.9932	0.9925	
	A	0.86	0.85	0.87	0.88	0.89	0.89	0.89	
	B	1.48	1.37	1.13	1.56	1.10	1.09	1.03	
B3LYP	R	0.9914	0.9914	0.995	0.9858	0.9958	0.9956	0.9951	
	A	0.90	0.87	0.89	0.90	0.91	0.91	0.91	
	B	0.79	0.91	0.63	1.12	0.54	0.55	0.48	
PBE1PBE	R	0.9864	0.9897	0.9933	0.9844	0.9936	0.9932	0.9929	
	A	0.88	0.86	0.88	0.89	0.90	0.90	0.90	
	B	1.11	1.05	0.77	1.28	0.70	0.71	0.66	

The results of calculations of proton nuclear magnetic shielding tensors for a number of molecules *in vacuo* are collected in Table 2, and compared with the experimental values. The data indicates that for all molecules except HF, the calculations carried out in the full STO(IIF)-3G$_{\mathrm{mag}}$ basis set shows the best agreement with experimental data, especially in combination with BP86 functional, and, in a few cases, with PBE1PBE functional.

Table 2

^{1}H nuclear magnetic shielding tensors σ (ppm) and the parameters of the linear regression equation σ_{expt}=A* σ_{calc} + B

Method	STO(II*F*)-3G$_{\mathrm{mag}}$	STO(IIM)-3G$_{\mathrm{mag}}$	STO(IIV)-3G$_{\mathrm{mag}}$	STO$^{\#\#}$-3G$_{\mathrm{mag}}$	pc-2	pcJ-2	aug-cc-pVTZ	Experiment
1	2	3	4	5	6	7	8	9
				C_2H_6				
HF	30.99	31.57	31.58	31.52	31.31	31.25	31.31	29.86 [28]
BP86	30.12	30.71	30.71	30.62	30.40	30.26	30.43	
B3LYP	30.50	31.13	31.14	31.01	30.79	30.76	30.82	
PBE1PBE	30.33	30.92	30.93	30.87	30.68	30.64	30.69	
				C_2H_4				
HF	26.12	26.75	26.73	26.51	26.57	26.48	26.54	25.43 [29]
BP86	25.18	25.90	25.88	25.63	25.58	25.53	25.58	
B3LYP	25.58	26.34	26.33	25.99	25.99	25.94	25.99	
PBE1PBE	25.33	26.01	25.99	25.78	25.75	25.69	25.73	

Table 2 (continuing)

1		2	3	4	5	6	7	8	9
					C_2H_2				
HF		29.74	30.99	31.09	30.17	30.76	30.65	30.72	29.28 [30]
BP86		29.25	30.40	30.49	29.72	30.18	30.14	30.18	
B3LYP		29.60	30.91	31.00	30.00	30.53	30.49	30.54	
PBE1PBE		29.39	30.49	30.58	29.82	30.34	30.27	30.31	
					CH_4				
HF		31.19	31.91	31.93	31.68	31.48	31.71	31.77	30.61 [31. 32]
BP86		30.64	31.47	31.48	31.03	31.21	31.18	31.23	
B3LYP		30.93	31.82	31.83	31.32	31.49	31.46	31.51	
PBE1PBE		30.78	31.56	31.58	31.21	31.39	31.34	31.39	
					H_2O				
HF		30.33	31.25	31.22	30.54	31.31	31.14	31.33	30.20 [33]
BP86		30.16	30.86	30.82	30.12	30.97	30.87	30.99	
B3LYP		30.20	30.97	30.94	30.22	31.05	30.93	31.09	
PBE1PBE		30.22	30.98	30.95	30.30	31.09	30.97	31.12	
					NH_3				
HF		31.46	32.44	32.46	31.78	32.10	31.97	32.09	30.68 [31. 32]
BP86		30.92	31.88	31.91	31.04	31.55	31.47	31.53	
B3LYP		31.11	32.14	32.16	31.24	31.76	31.68	31.75	
PBE1PBE		31.09	32.05	32.07	31.31	31.74	31.65	31.73	
					HF				
HF		28.84	28.94	28.65	28.39	29.19	27.25	29.20	29.20 [33]
BP86		29.05	29.14	28.84	29.60	29.45	29.32	29.44	
B3LYP		28.93	29.04	28.73	29.33	29.30	29.16	29.33	
PBE1PBE		28.99	29.10	28.80	29.24	29.35	29.22	29.38	
HF	R	0.9661	0.9365	0.9172	0.9156	0.9617	0.8445	0.966	
	A	0.94	0.85	0.81	0.84	0.91	0.68	0.9	
	B	1.28	3.47	4.7	3.99	1.63	8.74	2.03	
BP86	R	0.9977	0.9813	0.9686	0.9911	0.9947	0.9934	0.9948	
	A	0.93	0.88	0.85	0.96	0.89	0.89	0.89	
	B	2.11	2.93	3.79	0.9	2.79	2.8	2.81	
B3LYP	R	0.9884	0.9572	0.9394	0.9788	0.9848	0.9817	0.9854	
	A	0.94	0.86	0.82	0.95	0.9	0.89	0.9	
	B	1.55	3.24	4.38	0.81	2.3	2.43	2.3	
PBE1PBE	R	0.9942	0.9754	0.9619	0.9855	0.9906	0.9893	0.9916	
	A	0.92	0.86	0.83	0.93	0.88	0.88	0.88	
	B	2.22	3.32	4.22	1.62	2.99	3.06	3.01	

Conclusion

The new approach to the development of physically adapted basis set of atomic orbitals for the calculations of the magnetic properties of molecules which is based on the obtaining the second-order correction functions by the solution of nonhomogeneous Schrödinger equation for the model problem of "one-electron atom in a uniform external field" has been proposed and tested in this paper.

The obtained results of calculations of the magnetic susceptibility and the tensors of ^1H nuclear magnetic shielding have demonstrated good agreement with the experimental data.

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