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ORIGINAL PAPER

On the potential application of DFT methods in predicting the interaction-induced electric properties of molecular complexes. Molecular H-bonded chains as a case of study

**Agnieszka Zawada · Anna Kaczmarek-Kędziera ·
Wojciech Bartkowiak**

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Abstract A detailed analysis of the selected DFT functionals for the calculations of interaction-induced dipole moment, polarizability and first-order hyperpolarizability has been carried out. The hydrogen-bonded model chains consisting of HF, H_2CO and H_3N molecules have been chosen as a case study. The calculations of the components of the static electric properties using the diffuse Dunning's basis set (aug-cc-pVDZ) have been performed employing different types of density functionals (B3LYP, LC-BLYP, PBE0, M06-2X and CAM-B3LYP). Obtained results have been compared with those gained at the CCSD(T) level of theory. The counterpoise correction scheme, namely site-site function counterpoise, has been applied in order to eliminate basis set superposition error. The performed tests allow to conclude that the DFT functionals can provide a useful tool for prediction of the interaction-induced electric properties, however a caution has to be urged to their decomposition to the two- and many-body terms.

Keywords Density functional theory · Hydrogen bond · (Hyper) polarizability · Interaction-induced electric property · Many-body effects

A. Zawada (✉) · W. Bartkowiak
Institute of Physical and Theoretical Chemistry,
University of Technology,
Wybrzeże Wyspiańskiego 27,
50-370 Wroclaw, Poland
e-mail: agnieszka.zawada@pwr.wroc.pl

A. Kaczmarek-Kędziera
Faculty of Chemistry, Nicolaus Copernicus University,
Gagarina 7,
87-100 Torun, Poland

Introduction

Intermolecular interactions can significantly modify the properties of the investigated systems. Therefore, they continuously remain of interest for non-linear optics, nanoelectronics, biotechnology and many other fields of science. From the point of view of material science, interaction-induced electric properties for hydrogen-bonded systems could be of particular importance. However, systems that become relevant as novel materials are usually composed of more than several light atoms and therefore high-level calculations of their properties are prohibitively expensive. Thus, cheaper alternatives are sought. One of them appears to be the density functional theory (DFT). The great abundance of the various available DFT functionals allows to extend the investigations to the systems of hundreds of atoms and the wide range of analyzed properties.

It is known that the molecular electric properties can be reproduced by DFT methods with good accuracy [1–12]. However, one should bear in mind that for several classes of systems of importance to the non-linear optics, for instance long π-conjugated polymer chains as well as push-pull systems with significant charge transfer, such calculations lead to significant deterioration in the accuracy of the results [13–15]. Still, not much care has been devoted to the interaction-induced increments to dipole moments and (hyper)polarizabilities calculated beyond the wave function theory. Sparse data regard mostly rare gas heterodiatoms [16–19]. Only recently, various DFT functionals have been tested for the series of hydrogen-bonded dimers: water dimer, HF dimer and H_2 CO…HF [20]. Although there is no unambiguous answer to the question which functional is best for interaction-induced electric properties, it is quite easy to reproduce the CCSD(T) results for investigated systems with DFT methods with satisfactory accuracy [20]. Regarding the gathered information, further studies seem necessary in order to generalize such an observation.

The aim of the present study is to verify the applicability of the DFT formalism also for the interaction-induced electric properties of the longer hydrogen-bonded chains. The HF linear chain, H_2CO crystal structure and $H_3N\ldots(HF)_n$ complex are investigated up to five units in the system. The chosen structures were previously investigated at an angle of the many-body contributions to the (non)linear electric response with second order Møller-Plesset perturbation theory and the many-body interactions in these systems proved to be significant [21, 22].

The performance of the DFT functionals is tested against the CCSD(T) data that provide the reference level. In order to keep the consistency with the previous study [20], the same exchange-correlation functionals have been applied here: B3LYP [23–26] and PBE0 [27] as conventional hybrids, LC-BLYP [28] as a long-range corrected functional and M06-2X hybrid meta functional [29]. Additionally, this set was appended by the B3LYP long-range corrected modification (CAM-B3LYP) [30] for which we expect to improve the accuracy of the results toward reference data.

Methodology

The subject of the present study are hydrogen-bonded complexes, namely: linear $HF\cdots(HF)_n$, crystalline $H_2CO\cdots(H_2CO)_n$ and linear $H_3N\cdots(HF)_n$, for which n=1–4. The structures of linear $HF\cdots(HF)_n$ [31] and $H_3N\cdots(HF)_n$ [21] chains have been obtained based on gas-phase monomer geometries optimized at the MP2/6-31G(d,p) level of theory. Moreover, the intermonomer distance which corresponds to the separation in the linear dimer has been optimized at the very same level of theory. On the other hand, the geometry of the $H_2CO\cdots(H_2CO)_n$ chain refers to that found in the formaldehyde crystal [32]. The analyzed molecular complexes of maximal size are presented in Fig. 1.

All calculations of the static electric molecular properties were carried out at the SCF-HF, MP2, CCSD(T), B3LYP, PBE0, LC-BLYP, M06-2X and CAM-B3LYP level of theory. Values of the electric dipole (hyper) polarizability tensors have been obtained using the finite field (FF) method [33, 34] by numerical differentiation of energy with respect to external electric field (F). Relying on our previous research [21, 22] the electric field of the strength 0.001 a.u. has been chosen for further calculations to ensure the numerical stability of the FF procedure.

Interaction-induced properties ΔP for the investigated systems were obtained in a supermolecular manner:

$$\Delta P = P_{12\ldots n} - \sum_{i=1}^{n} P_i, \tag{1}$$

where $P_{12\ldots n}$ and P_i stands for the magnitude of the property for the n-body system and its constituents, respectively. In order to make the consistent comparison of electric properties for the whole set of studied systems, the following values of the electric properties are discussed:

$$|\mu| = \sqrt{\mu_x^2+\mu_y^2+\mu_z^2}, \tag{2}$$

$$\alpha_0 = \frac{1}{3}\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right), \tag{3}$$

$$\beta_\mu = \frac{\beta_x\mu_x + \beta_y\mu_y + \beta_z\mu_z}{|\mu|}, \tag{4}$$

where

$$\beta_i = \frac{3}{5}\cdot \sum_{j=x,y,z} \beta_{ijj} \tag{5}$$

and the Kleinman symmetry is satisfied.

The values of static electric properties obtained within the supermolecular approach together with basis set of finite

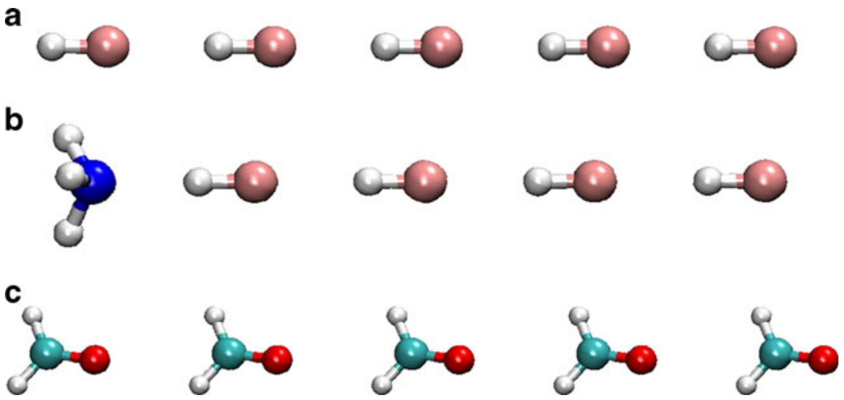

Fig. 1 Structure of investigated complexes of maximal length

size might suffer from the basis set superposition error [35, 36]. Due to the fact that the first-order hyperpolarizability is the most sensitive to the choice of the basis set of all the properties analyzed here [35, 36], the correction for BSSE has been included according to the site-site function counterpoise scheme [37]. The total interaction-induced counterpoise-corrected electric property $\Delta_{total}P^{CP}$ has been decomposed into:

$$\Delta_{total}P^{CP} = \sum_{i<j}\Delta_{ij}P(1\ldots n) + \sum_{i<j<k}\Delta_{ijk}P(1\ldots n) + \ldots + \Delta_{1\ldots n}P(1\ldots n), \quad (6)$$

Table 1 The values of the electric properties and their counterpoise corrected interaction-induced counterparts [a.u.] for the hydrogen-bonded linear HF⋯(HF)$_n$ complexes. The subsequent columns contain the information about the chain length n, the absolute value of the static dipole moment for the whole chain $|\mu|(0)$, the total interaction-induced dipole moment $\Delta|\mu|(0)$ and its contributions: two- and many-body, static polarizability $\alpha_0(0)$, the total interaction-induced polarizability $\Delta\alpha_0(0)$ and its two- and many-body components, first order hyperpolarizability $\beta_\mu(0)$, the total interaction-induced hyperpolarizability $\Delta\beta_\mu(0)$ and its two- and many-body components

	$\|\mu\|(0)$	$\Delta\|\mu\|(0)$			$\alpha_0(0)$	$\Delta\alpha_0(0)$			$\beta_\mu(0)$	$\Delta\beta_\mu(0)$		
n		Total	2-body	M-body		Total	2-body	M-body		Total	2-body	M-body
CCSD(T)												
1	1.5858	0.1730	0.1730	–	10.000	0.048	0.048	–	−11.67	4.32	4.32	–
2	2.4985	0.3789	0.3619	0.0170	15.139	0.177	0.119	0.058	−11.65	11.40	9.45	1.95
3	3.4218	0.5952	0.5554	0.0398	20.305	0.334	0.194	0.140	−10.63	19.64	14.79	4.85
4	4.3494	0.8159	0.7510	0.0649	25.482	0.503	0.270	0.233	−9.16	28.37	20.21	8.16
MP2												
1	1.5982	0.1739	0.1739	–	10.048	0.034	0.034	–	−10.97	4.18	4.18	–
2	2.5176	0.3810	0.3640	0.0170	15.201	0.146	0.090	0.056	−10.61	11.28	9.45	1.83
3	3.4477	0.5985	0.5589	0.0396	20.379	0.284	0.149	0.135	−9.43	19.31	14.83	4.48
4	4.3820	0.8203	0.7557	0.0646	25.568	0.434	0.210	0.224	−7.83	27.80	20.29	7.51
SCF-HF												
1	1.6931	0.1677	0.1677	–	8.893	0.019	0.019	–	−9.61	3.17	3.17	–
2	2.6527	0.3648	0.3509	0.0139	13.432	0.094	0.055	0.039	−10.49	8.12	6.97	1.15
3	3.6216	0.5711	0.5388	0.0323	17.989	0.188	0.094	0.094	−10.89	13.62	10.85	2.77
4	4.5942	0.7812	0.7286	0.0526	22.555	0.290	0.134	0.156	−11.06	19.36	14.76	4.60
B3LYP												
1	1.5976	0.1827	0.1827	–	10.458	0.096	0.096	–	−12.03	3.44	3.44	–
2	2.5251	0.4018	0.3818	0.0200	15.854	0.277	0.211	0.066	−10.49	11.86	8.08	3.78
3	3.4642	0.6323	0.5858	0.0465	21.280	0.490	0.327	0.163	−7.14	22.17	12.71	9.46
4	4.4079	0.8674	0.7918	0.0756	26.720	0.718	0.445	0.273	−3.17	33.29	18.03	15.26
LC-BLYP												
1	1.6152	0.1857	0.1857	–	10.833	0.081	0.081	–	−9.33	5.00	5.00	–
2	2.5546	0.4087	0.3884	0.0203	16.423	0.259	0.182	0.077	−5.99	14.40	11.55	2.85
3	3.5060	0.6436	0.5961	0.0475	22.046	0.472	0.287	0.185	−1.24	25.47	18.33	7.14
4	4.4624	0.8834	0.8059	0.0775	27.683	0.702	0.392	0.310	4.19	37.30	25.28	12.02
PBE0												
1	1.5989	0.1791	0.1791	–	10.237	0.101	0.101	–	−11.14	3.69	3.69	–
2	2.5236	0.3934	0.3743	0.0191	15.521	0.283	0.221	0.062	−9.72	11.45	8.11	3.34
3	3.4596	0.6189	0.5743	0.0446	20.835	0.497	0.343	0.154	−6.76	21.41	13.39	8.02
4	4.4001	0.8488	0.7762	0.0726	26.163	0.724	0.466	0.258	−3.20	31.80	18.42	13.38
M06-2X												
1	1.6097	0.1752	0.1752	–	9.870	0.096	0.096	–	−8.97	3.09	3.09	–
2	2.5363	0.3841	0.3661	0.0180	14.958	0.268	0.214	0.054	−7.65	9.90	7.09	2.81
3	3.4735	0.6035	0.5617	0.0418	20.074	0.469	0.335	0.134	−5.02	18.10	11.69	6.41
4	4.4151	0.8273	0.7593	0.0680	25.202	0.682	0.458	0.224	−1.76	26.96	15.99	10.97
CAM-B3LYP												
1	1.6161	0.1814	0.1814	–	10.355	0.079	0.079	–	−10.15	4.22	4.22	–
2	2.5516	0.3984	0.3793	0.0191	15.691	0.243	0.177	0.066	−8.15	12.63	10.06	2.57
3	3.4985	0.6267	0.5821	0.0446	21.055	0.440	0.278	0.162	−4.76	22.66	16.28	6.38
4	4.4500	0.8595	0.7869	0.0726	26.434	0.650	0.380	0.270	−0.78	32.94	21.24	11.70

Table 2 The values of the electric properties and their counterpoise corrected interaction-induced counterparts [a.u.] for the hydrogen-bonded linear $H_3N\cdots(HF)_n$ complexes. The subsequent columns contain the information about the chain length n, the absolute value of the static dipole moment for the whole chain |μ|(0), the total interaction-induced dipole moment Δ|μ|(0) and its contributions: two- and many-body, static polarizability $\alpha_0(0)$, the total interaction-induced polarizability $\Delta\alpha_0(0)$ and its two- and many-body components, first order hyperpolarizability $\beta_\mu(0)$, the total interaction-induced hyperpolarizability $\Delta\beta_\mu(0)$ and its two- and many-body components

	|μ|(0)	Δ|μ|(0)			$\alpha_0(0)$	$\Delta\alpha_0(0)$			$\beta_\mu(0)$	$\Delta\beta_\mu(0)$		
n		Total	2-body	M-body		Total	2-body	M-body		Total	2-body	M-body
CCSD(T)												
1	1.7256	0.4294	0.4294	–	18.366	−0.693	−0.693	–	−39.35	−8.38	−8.38	–
2	2.6984	0.6948	0.6443	0.0505	23.640	−0.436	−0.538	0.102	−25.03	14.29	13.37	0.92
3	3.6379	0.9273	0.8434	0.0839	28.875	−0.214	−0.451	0.237	−17.02	29.66	22.13	7.53
4	4.5714	1.1538	1.0410	0.1128	34.076	−0.021	−0.372	0.351	−12.91	41.19	28.81	12.38
MP2												
1	1.7368	0.4271	0.4271	–	18.415	−0.770	−0.770	–	−39.61	−9.85	−9.85	–
2	2.7159	0.6930	0.6436	0.0494	23.687	−0.545	−0.634	0.089	−26.21	11.29	11.39	−0.10
3	3.6620	0.9263	0.8441	0.0822	28.928	−0.348	−0.562	0.214	−18.79	25.60	20.22	5.38
4	4.6022	1.1538	1.0430	0.1108	34.139	−0.177	−0.498	0.321	−14.89	36.53	26.96	9.57
SCF-HF												
1	1.7939	0.3987	0.3987	–	16.655	−0.621	−0.621	–	−23.72	−16.77	−16.77	–
2	2.8031	0.6446	0.6045	0.0401	21.282	−0.459	−0.532	0.073	−16.45	7.43	7.21	0.22
3	3.7850	0.8636	0.7972	0.0664	25.881	−0.325	−0.484	0.159	−13.23	16.47	13.17	3.30
4	4.7624	1.0783	0.9889	0.0894	30.461	−0.209	−0.441	0.232	−12.10	23.57	17.87	5.70
B3LYP												
1	1.7604	0.4575	0.4575	–	18.935	−0.721	−0.721	–	−43.48	−11.45	−11.45	–
2	2.7526	0.7407	0.6833	0.0574	24.497	−0.382	−0.483	0.101	−18.93	21.84	23.24	−1.40
3	3.7094	0.9889	0.8930	0.0959	30.023	−0.075	−0.350	0.275	−3.34	44.54	32.39	12.15
4	4.6598	1.2305	1.1015	0.1290	35.500	0.190	−0.256	0.446	5.74	61.27	38.43	22.84
LC-BLYP												
1	1.7999	0.4579	0.4579	–	19.100	−0.750	−0.750	–	−33.61	−13.74	−13.74	–
2	2.8026	0.7436	0.6879	0.0557	24.827	−0.440	−0.537	0.097	−15.04	12.66	15.18	−2.52
3	3.7714	0.9958	0.9013	0.0945	30.533	−0.149	−0.416	0.267	−2.17	32.25	26.10	6.15
4	4.7342	1.2420	1.1133	0.1287	36.201	0.110	−0.306	0.416	6.40	47.47	34.45	13.02
PBE0												
1	1.7639	0.4572	0.4572	–	18.597	−0.641	−0.641	–	−39.45	−9.60	−9.60	–
2	2.7525	0.7346	0.6788	0.0558	24.049	−0.297	−0.397	0.100	−17.41	20.46	21.90	−1.44
3	3.7059	0.9772	0.8842	0.0930	29.455	0.004	−0.260	0.264	−3.91	41.06	31.23	9.83
4	4.6528	1.2135	1.0882	0.1253	34.816	0.265	−0.132	0.397	3.92	55.90	37.61	18.29
M06-2X												
1	1.7679	0.4466	0.4466	–	18.054	−0.594	−0.594	–	−32.85	−11.90	−11.90	–
2	2.7543	0.7146	0.6633	0.0513	23.279	−0.286	−0.365	0.079	−16.52	10.90	12.87	−1.97
3	3.7077	0.9500	0.8641	0.0859	28.467	−0.016	−0.227	0.211	−6.65	26.41	20.61	5.80
4	4.6552	1.1795	1.0637	0.1158	33.620	0.223	−0.102	0.325	−0.74	38.02	25.32	12.70
CAM-B3LYP												
1	1.7808	0.4493	0.4493	–	18.602	−0.696	−0.696	–	−34.74	−10.67	−10.67	–
2	2.7778	0.7272	0.6731	0.0541	24.078	−0.396	−0.497	0.101	−16.46	15.27	15.76	−0.49
3	3.7414	0.9721	0.8814	0.0907	29.525	−0.124	−0.382	0.258	−4.71	33.86	25.55	8.31
4	4.6991	1.2111	1.0884	0.1227	34.932	0.116	−0.275	0.391	2.53	47.70	31.84	15.86

Table 3 The values of the electric properties and their counterpoise corrected interaction-induced counterparts [a.u.] for the hydrogen-bonded crystalline $H_2CO\cdots(H_2CO)_n$ complexes. The subsequent columns contain the information about the chain length n, the absolute value of the static dipole moment for the whole chain $|\mu|(0)$, the total interaction-induced dipole moment $\Delta|\mu|(0)$ and its contributions: two- and many-body, static polarizability $\alpha_0(0)$, the total interaction-induced polarizability $\Delta\alpha_0(0)$ and its two- and many-body components, first order hyperpolarizability $\beta_\mu(0)$, the total interaction-induced hyperpolarizability $\Delta\beta_\mu(0)$ and its two- and many-body components

n	$\|\mu\|(0)$	$\Delta\|\mu\|(0)$			$\alpha_0(0)$	$\Delta\alpha_0(0)$			$\beta_\mu(0)$	$\Delta\beta_\mu(0)$		
		Total	2-body	M-body		Total	2-body	M-body		Total	2-body	M-body
CCSD(T)												
1	2.0358	0.1432	0.1432	–	34.868	0.397	0.397	–	−93.09	9.40	9.40	–
2	3.1540	0.3158	0.3027	0.0131	52.732	0.959	0.846	0.113	−129.23	23.59	21.21	2.38
3	–	–	–	–	–	–	–	–	–	–	–	–
4	–	–	–	–	–	–	–	–	–	–	–	–
MP2												
1	2.0396	0.1418	0.1418	–	34.901	0.391	0.391	–	−71.84	12.37	12.37	–
2	3.1592	0.3131	0.2999	0.0132	52.787	0.956	0.837	0.119	−95.61	29.77	27.72	2.05
3	4.2881	0.4937	0.4628	0.0309	70.728	1.577	1.297	0.280	−117.49	49.05	43.62	5.43
4	5.4208	0.6781	0.6277	0.0504	88.693	2.223	1.764	0.459	−138.57	69.12	59.94	9.18
SCF-HF												
1	2.4631	0.1651	0.1651	–	33.078	0.322	0.322	–	−93.10	1.82	1.82	–
2	3.8093	0.3631	0.3492	0.0139	49.954	0.774	0.689	0.085	−136.25	5.06	4.62	0.44
3	5.1658	0.5713	0.5387	0.0326	66.871	1.268	1.069	0.199	−178.80	8.94	7.61	1.33
4	6.5265	0.7837	0.7307	0.0530	83.805	1.780	1.455	0.325	−221.06	13.11	10.68	2.43
B3LYP												
1	2.0993	0.1527	0.1527	–	35.794	0.439	0.439	–	−127.42	6.30	6.30	–
2	3.2562	0.3371	0.3225	0.0146	54.148	1.044	0.921	0.123	−176.60	23.66	16.38	7.28
3	4.4231	0.5314	0.4974	0.0340	72.557	1.707	1.416	0.291	−222.09	44.70	27.14	17.56
4	5.5941	0.7298	0.6743	0.0555	90.990	2.394	1.917	0.477	−266.02	67.31	38.28	29.03
LC-BLYP												
1	2.1647	0.1557	0.1557	–	35.829	0.444	0.444	–	−94.81	10.29	10.29	–
2	3.3566	0.3437	0.3290	0.0147	54.214	1.063	0.937	0.126	−129.63	27.18	23.88	3.30
3	4.5587	0.5420	0.5075	0.0345	72.656	1.743	1.445	0.298	−161.90	46.63	38.19	8.44
4	5.7649	0.7445	0.6882	0.0563	91.121	2.447	1.959	0.488	−193.03	67.22	52.77	14.45
PBE0												
1	2.0949	0.1499	0.1499	–	35.236	0.453	0.453	–	−118.82	6.06	6.06	–
2	3.2476	0.3307	0.3166	0.0141	53.308	1.068	0.950	0.118	−165.99	20.86	15.13	5.73
3	4.4100	0.5213	0.4882	0.0331	71.433	1.739	1.460	0.279	−210.13	38.67	24.83	13.84
4	5.5764	0.7158	0.6618	0.0540	89.581	2.433	1.975	0.458	−252.98	57.78	34.79	22.99
M06-2X												
1	2.1365	0.1473	0.1473	–	34.593	0.440	0.440	–	−100.17	7.74	7.74	–
2	3.3083	0.3251	0.3114	0.0137	52.325	1.040	0.925	0.115	−139.83	21.32	17.78	3.54
3	4.4897	0.5125	0.4804	0.0321	70.108	1.694	1.424	0.270	−177.40	37.01	28.40	8.61
4	5.6750	0.7039	0.6516	0.0523	87.913	2.369	1.928	0.441	−214.09	53.56	39.11	14.45
CAM-B3LYP												
1	2.1713	0.1547	0.1547	–	35.232	0.417	0.417	–	−100.59	9.14	9.14	–
2	3.3655	0.3411	0.3268	0.0143	53.288	0.999	0.880	0.119	−139.12	24.75	21.29	3.46
3	4.5697	0.5376	0.5040	0.0336	71.397	1.638	1.357	0.281	−175.29	42.73	33.92	8.81
4	5.7780	0.7382	0.6834	0.0548	89.529	2.300	1.840	0.456	−210.36	61.83	46.83	15.00

where the first summation includes all the two-body terms $\Delta_{ij}P(1\ldots n)$, the second one - all the three-body terms $\Delta_{ijk}P(1\ldots n)$ and the last term $\Delta_{1\ldots n}P(1\ldots n)$ contains the n-body interaction contribution.

The relative error of the investigated properties in different methods has been estimated with respect to the CCSD(T) calculations via:

$$\delta[\%] = \frac{\Delta P^{method} - \Delta P^{CCSD(T)}}{\Delta P^{CCSD(T)}} \cdot 100\%. \tag{7}$$

Similarly, the relative error for the BSSE-uncorrected data has been predicted as:

$$BSSE[\%] = \frac{\Delta P^{uncorr} - \Delta P^{corr}}{\Delta P^{corr}} \cdot 100\%. \tag{8}$$

All calculations have been performed with Gamess-US [38] and Gaussian09 [39] program packages with the aug-cc-pVDZ basis set [40, 41].

Results and discussion

Tables 1, 2 and 3 present the values of the electric properties and their interaction-induced contributions for all the investigated systems in different approaches. The corresponding relative errors (δ[%]) for $\Delta|\mu|(0)$, $\Delta\alpha_0(0)$, and $\Delta\beta_\mu(0)$ are plotted in Figs. 2, 3 and 4, respectively. For comparison the electric properties of the isolated units (HF, H_2CO and H_3N) are also provided in Table 4.

Dipole moment

The careful analysis of the gathered data for the interaction-induced dipole moments reveals quite a good performance of the tested DFT functionals. For most cases, the DFT results are of better quality than SCF-HF data. However, the exceptions are observed for linear HF and $H_3N\ldots(HF)_n$

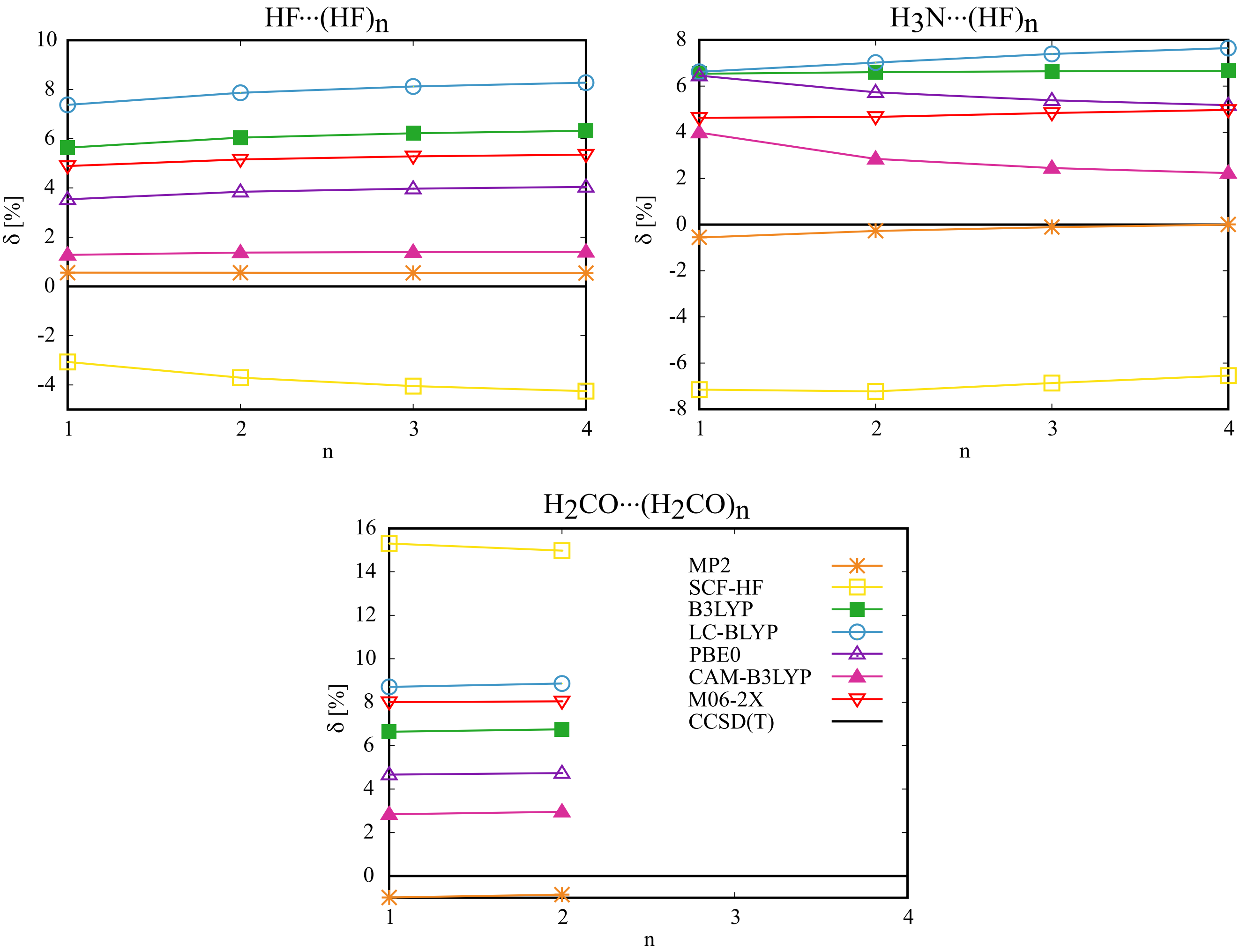

Fig. 2 The percentage relative errors of the approximation applied for estimation of the interaction-induced dipole moment with respect to the CCSD(T) results

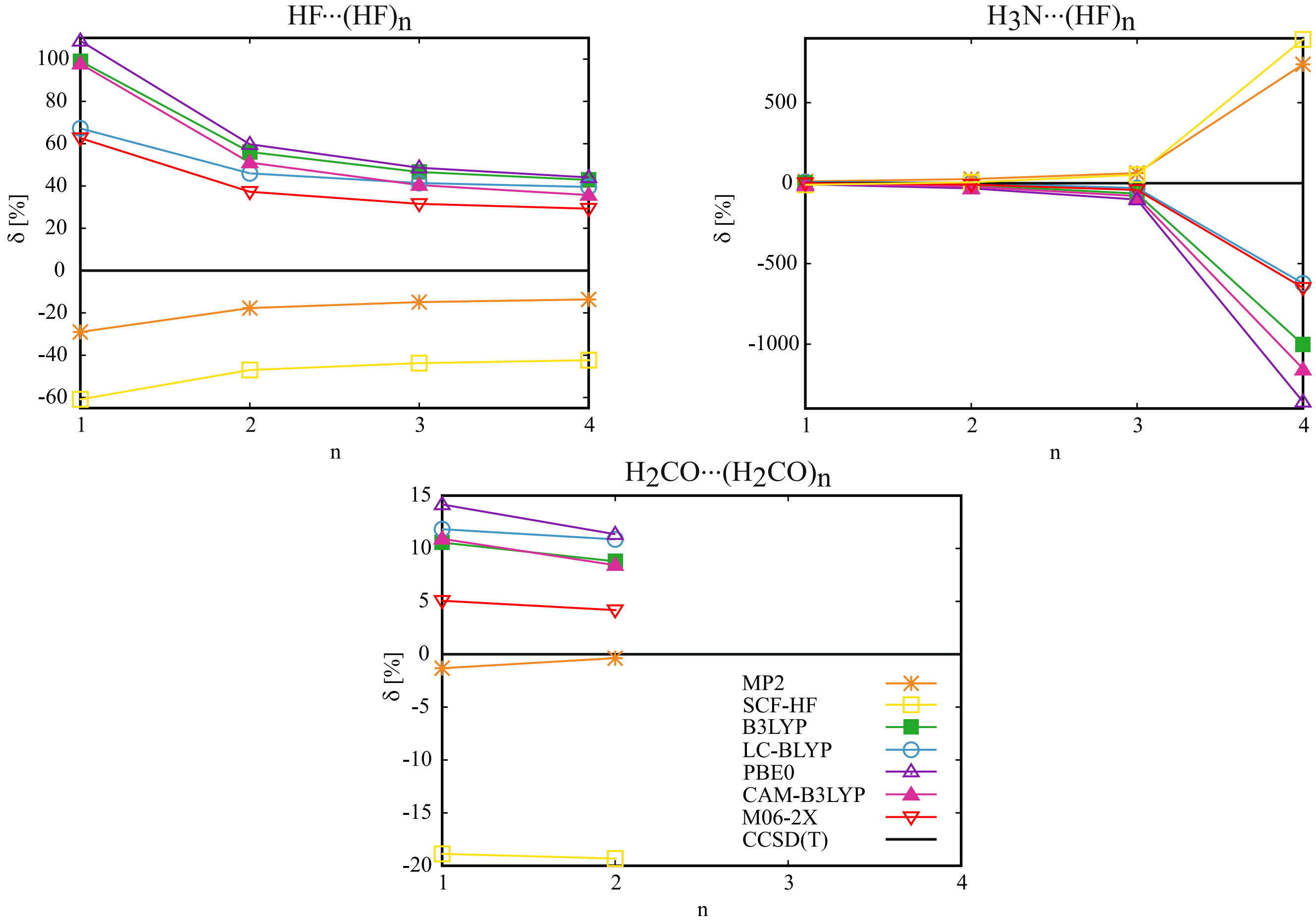

Fig. 3 The percentage relative errors of the approximation applied for estimation of the interaction-induced polarizability with respect to the CCSD(T) results

chains. In both cases LC-BLYP performs noticeably worse than SCF-HF approach with the relative error almost twice as large for the HF chain. Additionally, for the HF chain also the B3LYP functional and its long-range corrected version CAM-B3LYP demonstrate slight aggravation with respect to the SCF-HF approach. The relative error for the DFT calculations in all the investigated cases does not exceed 9%. The worst data are obtained with LC-BLYP, where the relative errors are between 7.5% and 8.5% and the best agreement with the CCSD(T) interaction-induced dipole moments is observed for the M06-2X functional (errors 1.5%-4%). It is worth mentioning that the relative error for the MP2 calculations does not surpass 1%.

The comparison of the data presented in Fig. 2 shows that the relative error of the interaction-induced dipole moment remains approximately constant with the chain elongation for the HF and H_2CO complexes. On the other hand, the lengthening of the $H_3N\ldots(HF)_n$ system leads to the improvement of the M06-2X and PBE0 results - the errors decrease from 4% to 2% and from 6.5% to 5%, respectively. The opposite behavior is observed for the LC-BLYP data - the results worsen by more than 1% with increasing chain length.

The decomposition of the total interaction-induced dipole moment for the inspected complexes does not disclose any abrupt demeanor of the DFT results: The quality of the obtained two- and more-body components does not raise many reservations and therefore the DFT functionals tested in this study can be recommended for the many-body analysis of the interaction-induced dipole moment of the investigated complexes.

Polarizability

Due to the almost negligible non-additivity in the case of the polarizability of the analyzed molecular chains (interaction-induced polarizability less than 1 a.u. for linear chains and less than 2.5 a.u. for formaldehyde complex - below 2.8%) the detailed study of the obtained data is omitted. The relative errors for the interaction-induced polarizability are depicted in Fig. 3. For the HF chain the relative error decreases with chain elongation. The dramatic increase of

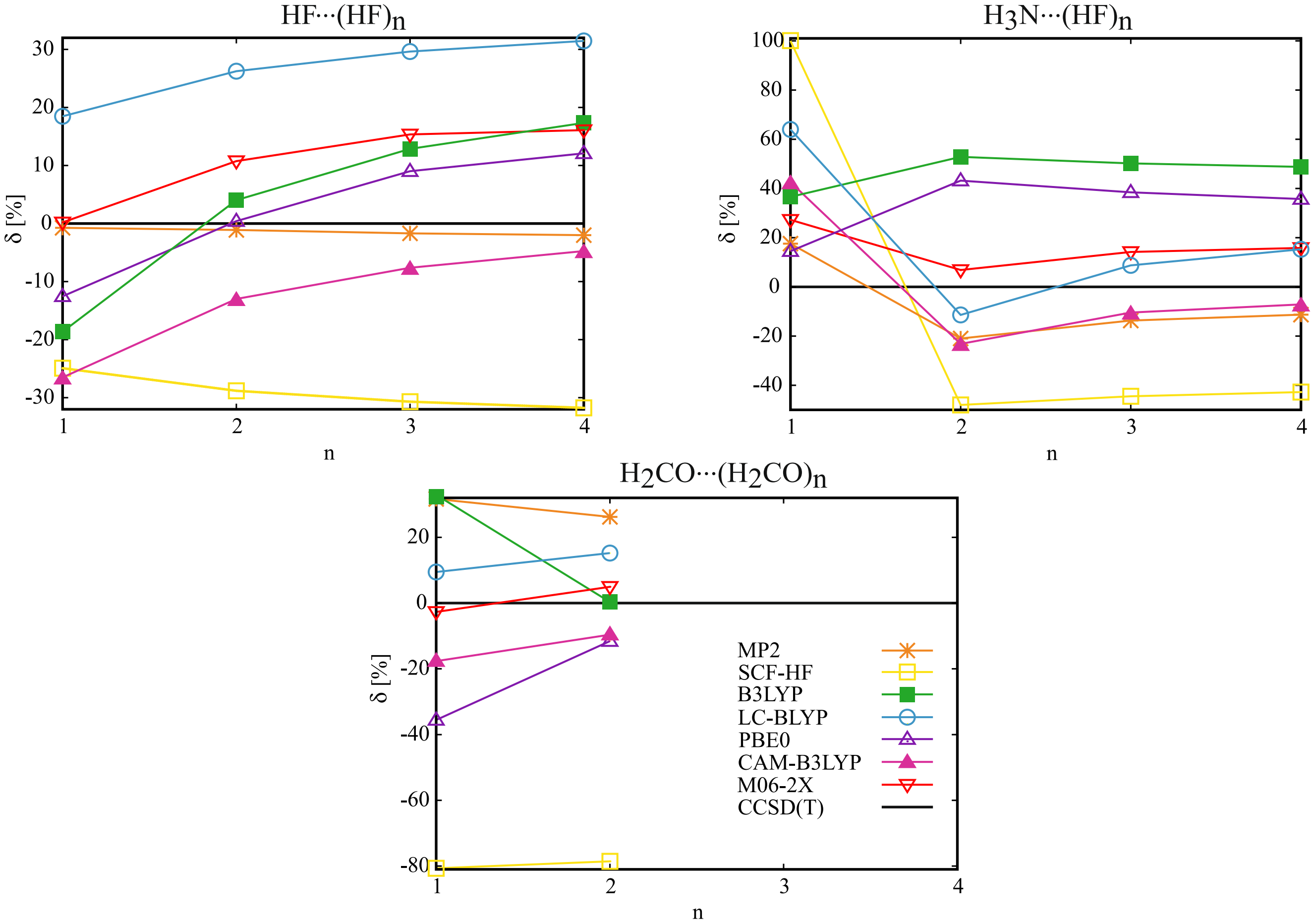

Fig. 4 The percentage relative errors of the approximation applied for estimation of the interaction-induced hyperpolarizability with respect to the CCSD(T) results

the error for the longest $H_3N\ldots(HF)_n$ complex should not be taken into account, since the interaction-induced increment for the CCSD(T) calculations of the five-membered chain accounts for only 0.06% of the total polarizability value. Therefore, the interaction-induced polarizability within for instance PBE0 approach, that makes up 0.76% of the total PBE0 polarizability for the longest chain, appears to be in large error with respect to the CCSD(T) data; however this still gives a very good predictive power for the total polarizability values.

The contribution from many-body terms increases with the chain elongation and for long chains it may exceed the two-body terms [21]. In the case of the $H_3N\ldots(HF)_n$ complexes, where the two- and many-body terms have opposite signs, the expansion of the chain leads from the negative interaction-induced polarizability that weakens the total response of the system, to the positive $\Delta\alpha_0$ for larger number of HF units, where the interaction-induced contribution additionally strengthens the total polarizability of the system. This tendency would be observed for all the investigated methods, however the applied DFT functionals predict the length of the chain for which $\Delta\alpha_0$ changes sign as smaller than respective CCSD(T), MP2 or SCF calculations. In other words, DFT overestimates the many-body terms with respect to the two-body contributions. This is however not a general observation for DFT functionals, since for the HF chains the propensity is opposite: DFT seems to underestimate slightly the many-body terms in comparison to the two-body contributions, and in the case of the H_2CO chains the agreement between all the applied methods for the ratio of the many-body to two-body contributions to interaction-induced polarizability is very good.

All the calculations lead to the conclusion that again the MP2 method gives good quality results. Additionally, the best-performing DFT functional is CAM-B3LYP.

Hyperpolarizability

According to the author's expectations and experiences [20, 42] the analysis of the DFT functionals assesment appeared to be most complex.

Figure 4 depicts the relative error for the interaction-induced hyperpolarizability. The worst quality results have

Table 4 The values of the electric properties [a.u.] of analyzed monomers

	HF	H_3N	H_2CO
		$|\mu|(0)$	
CCSD(T)	0.7059	0.5919	0.9470
MP2	0.7118	0.5999	0.9496
SCF-HF	0.7631	0.6350	1.1498
B3LYP	0.7063	0.5949	0.9740
LC-BLYP	0.7129	0.6249	1.0053
PBE0	0.7094	0.5993	0.9733
M06-2X	0.7168	0.6051	0.9954
CAM-B3LYP	0.7161	0.6129	1.0090
		α_0 (0)	
CCSD(T)	4.941	13.815	17.152
MP2	4.971	13.898	17.169
SCF-HF	4.409	12.652	16.321
B3LYP	5.145	14.194	17.584
LC-BLYP	5.337	14.231	17.595
PBE0	5.031	13.893	17.307
M06-2X	4.856	13.542	17.005
CAM-B3LYP	5.103	13.918	17.321
		β_μ (0)	
CCSD(T)	−8.89	−22.24	−52.11
MP2	−8.05	−20.56	−42.98
SCF-HF	−6.90	−10.71	−48.60
B3LYP	−8.72	−24.55	−66.95
LC-BLYP	−8.49	−13.76	−53.23
PBE0	−8.18	−21.45	−62.74
M06-2X	−6.72	−15.91	−54.62
CAM-B3LYP	−8.34	−17.08	−55.43

been obtained definitely with the SCF-HF approach - the errors ranging from 25% to 100%. For the formaldehyde complex the DFT functionals in general perform better than MP2 and the only exception is the PBE0 interaction-induced hyperpolarizability of the dimer. Taking MP2 approach as the suitable method for the incremental values estimation, one can treat its largest error (32% for the formaldehyde dimer) as an indicator for the satisfactory performance of the DFT functionals. For the linear HF chain all the investigated functionals achieve smaller errors than this limit. In the case of the formaldehyde complexes only PBE0 behaves worse for the dimer. Yet only two functionals lie in this range for the $H_3N\ldots(HF)_n$ system, namely M06-2X and CAM-B3LYP.

The addition of one unit to the investigated dimers has a significant influence on the quality of the obtained results. With the chain elongation for the HF complexes the relative errors of the DFT interaction-induced hyperpolarizability increase and in the case of PBE0 and B3LYP changes sign for trimer. Similar behavior might be expected for the M06-2X functional for chains longer than investigated. In other words, these functionals underestimate $\Delta\beta_\mu$ for HF dimer and overestimate it for longer chains. The opposite tendency is observed for the $H_3N\ldots(HF)_n$ complex. Here, the dramatic decrease of the relative error value is observed for the LC-BLYP, M06-2X and CAM-B3LYP functionals when going from $H_3N\ldots HF$ to $H_3N\ldots(HF)_2$. However, for longer complexes the error values stabilize. Thus, B3LYP, CAM-B3LYP and PBE0 give the overestimation of $\Delta\beta_\mu$ for all the analyzed lengths. LC-BLYP exhibits the underestimation of the $\Delta\beta_\mu$ value for the $H_3N\ldots(HF)_2$ and its overestimation besides. Moreover, M06-2X for three of four investigated $H_3N\ldots(HF)_n$ complexes underestimates $\Delta\beta_\mu$, however its relative errors could be expected to change sign again for the chains longer than investigated. Additionally the correct qualitative description of the total nonlinear response of the HF chain was achived by the DFT calculations, which is in contrary to the SCF-HF results (observe the increase of the β_μ to the absolute value).

The decomposition of the interaction-induced hyperpolarizability into the two- and more-body components reveals imperfections of the commonly applied hybrid functionals: B3LYP and PBE0. For all the investigated systems the many-body component calculated with these functionals are of poor quality with respect to the CCSD(T) reference data. Additionally, for the $H_3N\ldots(HF)_n$ systems also the two-body terms are not reproduced well. On the other hand, DFT reproduces well the sign change of the two-body terms in the $H_3N\ldots(HF)_n$ chains with the system elongation. For the many-body terms DFT (and MP2) also predicts the change of sign going from n=2 to n=3, however this effect is not present in the CCSD(T) reference results, when all the many-body terms are positive.

Comparison of the ratio of the many-body to the two-body terms in the case of the interaction-induced hyperpolarizability indicates its overestimation for the HF and H_2CO chains and good correspondence in the case of $H_3N\ldots(HF)_n$ complexes. Additionally, the mutual relations of the monomer properties and interaction-induced contributions causes the total hyperpolarizability β_μ to change signs for shorter HF and $H_3N\ldots(HF)_n$ chains within the DFT approaches than within the CCSD(T) calculations. This observation is consistent with the previously performed analysis for long HF chains [21].

Basis set superposition error

The estimated BSSE values for the investigated complexes are summarized in Tables 5, 6 and 7. It should be repeated that all the calculations have been carried out with the aug-cc-pVDZ basis set of the medium size.

Table 5 Interaction-induced electric properties for the hydrogen-bonded linear HF…$(HF)_n$ complexes with and without counterpoise correction and the basis set superposition error [%]

n	$\Delta\|\mu\|(0)$			$\Delta\alpha_0(0)$			$\Delta\beta_\mu(0)$		
	CP-cor	CP-uncor	BSSE	CP-cor	CP-uncor	BSSE	CP-cor	CP-uncor	BSSE
CCSD(T)									
1	0.1730	0.1739	0.52%	0.048	0.118	145.83%	4.32	6.10	41.20%
2	0.3789	0.3807	0.48%	0.177	0.316	78.53%	11.40	15.01	31.67%
3	0.5952	0.5980	0.47%	0.334	0.540	61.68%	19.64	24.92	26.88%
4	0.8159	0.8196	0.45%	0.503	0.777	54.47%	28.37	35.28	24.36%
MP2									
1	0.1739	0.1746	0.40%	0.034	0.106	211.76%	4.18	5.12	22.49%
2	0.3810	0.3823	0.34%	0.146	0.288	97.26%	11.28	13.52	19.86%
3	0.5985	0.6005	0.33%	0.284	0.495	74.30%	19.31	22.75	17.81%
4	0.8203	0.8231	0.34%	0.434	0.713	64.29%	27.80	32.39	16.51%
SCF-HF									
1	0.1677	0.1670	−0.42%	0.019	0.075	294.74%	3.17	4.18	31.86%
2	0.3648	0.3636	−0.33%	0.094	0.206	119.15%	8.12	10.20	25.62%
3	0.5711	0.5694	−0.30%	0.188	0.354	88.30%	13.62	16.69	22.54%
4	0.7812	0.7789	−0.29%	0.290	0.511	76.21%	19.36	23.42	20.97%
B3LYP									
1	0.1827	0.1850	1.26%	0.096	0.167	73.96%	3.44	5.41	57.27%
2	0.4018	0.4062	1.10%	0.277	0.418	50.90%	11.86	15.66	32.04%
3	0.6323	0.6389	1.04%	0.490	0.698	42.45%	22.17	27.74	25.12%
4	0.8674	0.8764	1.04%	0.718	0.993	38.30%	33.29	40.43	21.45%
LC-BLYP									
1	0.1857	0.1894	1.99%	0.081	0.158	95.06%	5.00	7.65	53.00%
2	0.4087	0.4159	1.76%	0.259	0.411	58.69%	14.40	19.47	35.21%
3	0.6436	0.6544	1.68%	0.472	0.696	47.46%	25.47	32.72	28.46%
4	0.8834	0.8978	1.63%	0.702	0.996	41.88%	37.30	46.63	25.01%
PBE0									
1	0.1791	0.1801	0.56%	0.101	0.174	72.28%	3.69	5.23	41.73%
2	0.3934	0.3954	0.41%	0.283	0.427	50.88%	11.45	14.83	29.52%
3	0.6189	0.6219	0.48%	0.497	0.709	42.66%	21.41	25.98	21.35%
4	0.8488	0.8530	0.49%	0.724	1.005	38.81%	31.80	37.72	18.62%
M06-2X									
1	0.1752	0.1762	0.57%	0.096	0.157	63.54%	3.09	4.47	44.66%
2	0.3841	0.3860	0.49%	0.268	0.388	44.78%	9.90	12.50	26.26%
3	0.6035	0.6065	0.50%	0.469	0.648	38.17%	18.10	21.86	20.77%
4	0.8273	0.8313	0.48%	0.682	0.919	34.75%	26.96	31.83	18.06%
CAM-B3LYP									
1	0.1814	0.1840	1.43%	0.079	0.148	87.34%	4.22	6.53	54.59%
2	0.3984	0.4034	1.26%	0.243	0.380	56.38%	12.63	16.87	33.57%
3	0.6267	0.6342	1.20%	0.440	0.642	45.91%	22.66	28.59	26.17%
4	0.8595	0.8697	1.19%	0.650	0.917	41.08%	32.94	40.91	24.20%

The relative error (BSSE[%]) arising from the lack of the BSSE correction for the dipole moment is usually smaller than 1% and only in the case of the linear HF chain for the LC-BLYP functional it reaches 2%. On these basis one can conclude that the counterpoise procedure has a negligible influence on the quality and quantity of the obtained interaction-induced dipole moment values for the studied complexes.

Table 6 Interaction-induced electric properties for the hydrogen-bonded $H_3N\ldots(HF)_n$ complexes with and without counterpoise correction and the basis set superposition error [%]

n	$\Delta\lvert\mu\rvert(0)$			$\Delta\alpha_0(0)$			$\Delta\beta_\mu(0)$		
	CP-cor	CP-uncor	BSSE	CP-cor	CP-uncor	BSSE	CP-cor	CP-uncor	BSSE
CCSD(T)									
1	0.4294	0.4277	−0.40%	−0.693	−0.390	−43.72%	−8.38	−8.22	−1.91%
2	0.6948	0.6945	−0.04%	−0.436	−0.057	−86.93%	14.29	14.98	4.83%
3	0.9273	0.9282	0.10%	−0.214	0.236	−210.28%	29.66	31.88	7.48%
4	1.1538	1.1557	0.16%	−0.021	0.497	−2466.67%	41.19	44.88	8.96%
MP2									
1	0.4271	0.4251	−0.47%	−0.770	−0.453	−41.17%	−9.85	−11.00	11.68%
2	0.6930	0.6924	−0.09%	−0.545	−0.153	−71.93%	11.29	10.44	−7.53%
3	0.9263	0.9267	0.04%	−0.348	0.117	−133.62%	25.60	25.90	1.17%
4	1.1539	1.1552	0.11%	−0.177	0.358	−302.26%	36.53	37.85	3.61%
SCF-HF									
1	0.3987	0.3958	−0.73%	−0.621	−0.406	−34.62%	−16.77	−6.11	−63.57%
2	0.6446	0.6420	−0.40%	−0.459	−0.188	−59.04%	7.43	8.05	8.34%
3	0.8636	0.8608	−0.32%	−0.325	0.003	−100.92%	16.47	18.17	10.32%
4	1.0783	1.0752	−0.29%	−0.209	0.174	−183.25%	23.57	26.20	11.16%
B3LYP									
1	0.4575	0.4592	0.37%	−0.721	−0.405	−43.83%	−11.45	−10.21	−10.83%
2	0.7407	0.7450	0.58%	−0.382	0.012	−103.14%	21.84	23.06	5.59%
3	0.9889	0.9956	0.68%	−0.075	0.393	−624.00%	44.54	47.37	6.35%
4	1.2305	1.2396	0.74%	0.190	0.725	281.58%	61.27	65.17	6.37%
LC-BLYP									
1	0.4579	0.4621	0.92%	−0.750	−0.468	−37.60%	−13.74	−11.36	−17.32%
2	0.7436	0.7519	1.12%	−0.440	−0.079	−82.05%	12.66	15.70	24.01%
3	0.9958	1.0078	1.21%	−0.149	0.290	−294.63%	32.25	37.06	14.91%
4	1.2420	1.2577	1.26%	0.110	0.620	463.64%	47.47	54.11	13.99%
PBE0									
1	0.4572	0.4552	−0.44%	−0.641	−0.327	−48.99%	−9.60	−9.82	2.29%
2	0.7346	0.7344	−0.03%	−0.297	0.094	−131.65%	20.46	20.40	−0.29%
3	0.9772	0.9783	0.11%	0.004	0.468	11600.00%	41.06	42.10	2.53%
4	1.2135	1.2158	0.19%	0.265	0.797	200.75%	55.90	58.10	3.94%
M06-2X									
1	0.4466	0.4461	−0.11%	−0.594	−0.345	−41.92%	−11.90	−10.22	−14.12%
2	0.7146	0.7158	0.17%	−0.286	0.024	−108.39%	10.90	12.83	17.71%
3	0.9500	0.9523	0.24%	−0.016	0.355	−2318.75%	26.41	29.42	11.40%
4	1.1795	1.1831	0.31%	0.223	0.652	192.38%	38.02	42.05	10.60%
CAM-B3LYP									
1	0.4493	0.4518	0.55%	−0.696	−0.419	−39.80%	−10.67	−9.32	−12.65%
2	0.7272	0.7327	0.75%	−0.396	−0.046	−88.38%	15.27	17.30	13.29%
3	0.9721	0.9803	0.84%	−0.124	0.297	−339.52%	33.86	37.39	10.43%
4	1.2111	1.2219	0.89%	0.116	0.601	418.10%	47.70	52.97	11.05%

The analysis of the relative BSSE for the linear HF and $H_3N\ldots(HF)_n$ complex is unreasonable due to the very small $\Delta\alpha_0$ values. However, for the formaldehyde chains the obtained results become more stable owing to the larger interaction-induced polarizability values than in the case of the remaining systems. Here, the relative BSSE changes from above 40% for short chains to almost 20% for longer chains. Nevertheless, again the influence of the interaction-induced

Table 7 Interaction-induced electric properties for the hydrogen-bonded crystalline $H_2CO\ldots(H_2CO)_n$ complexes with and without counterpoise correction and the basis set superposition error [%]

n	$\Delta\|\mu\|(0)$			$\Delta\alpha_0(0)$			$\Delta\beta_\mu(0)$		
	CP-cor	CP-uncor	BSSE	CP-cor	CP-uncor	BSSE	CP-cor	CP-uncor	BSSE
CCSD(T)									
1	0.1432	0.1418	−0.98%	0.397	0.563	41.81%	9.40	11.12	18.30%
2	0.3158	0.3130	−0.89%	0.959	1.275	32.95%	23.59	27.09	14.84%
3	–	–	–	–	–	–	–	–	–
4	–	–	–	–	–	–	–	–	–
MP2									
1	0.1418	0.1404	−0.99%	0.391	0.563	43.99%	12.37	14.13	14.23%
2	0.3131	0.3103	−0.89%	0.956	1.281	34.00%	29.77	33.34	11.99%
3	0.4937	0.4895	−0.85%	1.578	2.053	30.10%	49.05	54.44	10.99%
4	0.6781	0.6726	−0.81%	2.223	2.849	28.16%	69.12	76.35	10.46%
SCF-HF									
1	0.1651	0.1636	−0.91%	0.322	0.436	35.40%	1.82	4.10	125.27%
2	0.3631	0.3600	−0.85%	0.774	0.992	28.17%	5.06	9.54	88.54%
3	0.5713	0.5667	−0.81%	1.268	1.588	25.24%	8.94	15.59	74.38%
4	0.7837	0.7777	−0.77%	1.780	2.202	23.71%	13.11	21.92	67.20%
B3LYP									
1	0.1527	0.1512	−0.98%	0.439	0.627	42.82%	6.30	6.48	2.86%
2	0.3371	0.3341	−0.89%	1.044	1.397	33.81%	23.66	24.26	2.54%
3	0.5314	0.5270	−0.83%	1.707	2.222	30.17%	44.70	45.72	2.28%
4	0.7298	0.7239	−0.81%	2.394	3.072	28.32%	67.31	68.74	2.12%
LC-BLYP									
1	0.1557	0.1541	−1.03%	0.444	0.639	43.92%	10.29	11.65	13.22%
2	0.3437	0.3407	−0.87%	1.063	1.429	34.43%	27.18	30.05	10.56%
3	0.5420	0.5375	−0.83%	1.743	2.276	30.58%	46.63	51.01	9.39%
4	0.7445	0.7384	−0.82%	2.447	3.147	28.61%	67.22	73.11	8.76%
PBE0									
1	0.1499	0.1484	−1.00%	0.453	0.622	37.31%	6.06	6.66	9.90%
2	0.3307	0.3278	−0.88%	1.068	1.387	29.87%	20.86	22.25	6.66%
3	0.5213	0.5170	−0.82%	1.739	2.204	26.74%	38.67	40.85	5.64%
4	0.7158	0.7101	−0.80%	2.433	3.045	25.15%	57.78	60.74	5.12%
M06-2X									
1	0.1473	0.1457	−1.09%	0.440	0.584	32.73%	7.74	9.06	17.05%
2	0.3251	0.3221	−0.92%	1.040	1.311	26.06%	21.32	24.02	12.66%
3	0.5125	0.5080	−0.88%	1.694	2.088	23.26%	37.01	41.07	10.97%
4	0.7039	0.6979	−0.85%	2.369	2.888	21.91%	53.56	58.99	10.14%
CAM-B3LYP									
1	0.1547	0.1533	−0.90%	0.417	0.591	41.73%	9.14	10.26	12.25%
2	0.3411	0.3384	−0.79%	0.999	1.325	32.63%	24.75	27.16	9.74%
3	0.5376	0.5335	−0.76%	1.638	2.114	29.06%	42.73	46.42	8.64%
4	0.7382	0.7328	−0.73%	2.300	2.925	27.17%	61.83	66.77	7.99%

BSSE for the total value of the polarizability of the whole complex is negligible and the qualitative picture of the $\Delta\alpha_0$ changes with the chain elongation remains the same with or without the counterpoise correction.

The changes of the relative BSSE for the interaction-induced hyperpolarizability are parallel to these observed for the dipole moment, however here the absolute values of the errors decrease from 60% to 20% for HF chains and from 20% to 2% for formaldehyde chains with the chain elongation. Again, similarly as in the case of dipole moment and polarizability, the counterpoise procedure does not affect much the total qualitative picture. However, it cannot be neglected for the correct quantitative description of the interaction-induced hyperpolarizability of the investigated systems [35, 36].

Conclusions

The investigation of the electric properties of the hydrogen-bonded dimers [20] has shown that the M06-2X functional performed worst mainly for hyperpolarizability (compare HF dimer). However in the case of longer chains, it presents a serious advantage over any other tested functionals. Therefore, M06-2X appears to be the best for the description of the influence of the mutual interaction on the electric properties in the hydrogen-bonded chains. Similar performance can also be observed for the CAM-B3LYP functional. Although these conclusions were verified in the present contribution only for one basis set of the medium size (aug-cc-pVDZ), they should not differ dramatically for other basis set choices. The ordering of the functionals may vary, however the main conclusion of this work remain unchanged: DFT functionals can be applied succesfully for the investigation of the interaction-induced electric properties. One should however keep in mind that the DFT functional performance can also significantly depend on the nature of the intermolecular interactions and the conventional functionals are known to fail for systems governed by dispersion interaction [43–46].

It is also of importance for the complex systems, that the basis set superposition error in the case of interaction-induced dipole moment and polarizability is negligible. What is more for the first-order hyperpolarizability BSSE only has a noticable qualitative meaning, but the quantitative picture remains the same. This observation allows for instance to save a lot of effort in a rational design of novel materials. Further study on this topic is in progress.

The earlier studies suggest the possibility of estimating the electric properties for the large molecular aggregates based on the accurate description of molecular properties and approximate descripton of the interaction-induced contributions [21, 47]. Current findings allow to expect that calculations of molecular properties on high theory level (MP2 or CCSD(T)) supplemented by the interaction-induced increments accounted for in DFT could provide a relatively accurate and cheap alternative for regular post-Hartree-Fock predictions.

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