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REGULAR ARTICLE

On the basis set superposition error in supermolecular calculations of interaction-induced electric properties: many-body components

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Abstract In the present paper we analyze basis set superposition error (BSSE) removal methods from many-body components of interaction-induced electric properties. The Valiron–Mayer function counterpoise (VMFC), site–site function counterpoise (SSFC) and TB methods have been employed in order to obtain the incremental optical components of linear hydrogen fluoride clusters (HF)*n*, where *n* = {3,4}. Following Mierzwicki and Latajka, who have performed similar calculations for the interaction energy, we compare those three methods of eliminating BSSE using several Dunning's correlation consistent basis sets.

Keywords Basis set superposition error · Interaction-induced properties · Many-body components · NLO properties · (Hyper)polarizabilities

1 Introduction

The interaction energy and other interaction-induced properties obtained by supermolecular (SM) calculations are affected by basis set superposition error (BSSE), unless a complete basis set is used [1, 2]. This unphysical effect arises from the energy of each fragment in the complex being artificially lowered with respect to the energy of the isolated species, because of the presence of basis functions in adjacent fragments. Therefore, BSSE leads to a decrease in the SM interaction energy value (it is more negative) [3]. In the case of interaction-induced properties, this effect might be different (changes due to BSSE might be positive or negative).

The most commonly used procedure for avoiding BSSE in interaction energy calculations of dimeric subsystems is that proposed by Boys and Bernardi [4] and is known as a counterpoise correction (CP). It is well established and widely discussed that the CP correction gives correct values for BSSE [5], although some authors suggest using the largest possible basis set as the simplest way to diminish BSSE [3]. An in-depth discussion of the counterpoise theory can be found in reviews published by van Duijneveldt et al. [1, 6].

For the many-body components of interaction energy in the SM approach, three main schemes of BSSE removal have been proposed as an extension of the Boys–Bernardi method for dimers. These are the site–site function counterpoise (SSFC) method introduced by Wells and Wilson [7], the hierarchical counterpoise scheme of Valiron and Mayer [8], and the TB scheme proposed by Mierzwicki and Latajka [9]. Theoretical insight into the SSFC, VMFC, and TB methods are given in the next section. More methods exist for calculating BSSE-free interaction energies in many-body systems [7, 10]; however, they do not allow energy decomposition into *N*-body components and will not be discussed in the present paper. All the schemes mentioned have been compared with respect to removing BSSE from interaction energies [9] as well as structural and vibrational properties [11].

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The concept of interaction energy can be extended to analyze the influence of intermolecular interaction on other molecular properties, in particular optical and electric properties. The theoretical background for interaction-induced properties has been given in several important works [12–16]. Most of the calculated interaction-induced electric properties published to date refer to two-body van der Waals complexes [15, 17–30]; only a few contain results for many-body components [18, 31–35].

Similarly to the interaction energy calculations, the Boys–Bernardi CP correction is commonly used in order to obtain BSSE-free two-body interaction-induced electric properties. Unfortunately, only a few reports exist where corrected and uncorrected values are compared [3, 36]. These works generally state that the basis set superposition error in interaction-induced electric properties is rather small, but should be carefully considered.

In a previous letter [34] the authors compared BSSE-corrected (SSFC) and uncorrected interaction-induced components of the dipole moment and (hyper)polarizability for linear fluoroacetylene trimers. The main observation was that BSSE does not significantly affect the components of the interaction-induced dipole moment and polarizability. In the case of hyperpolarizability one should be more careful and provide suitable tests.

In the present paper we analyze BSSE removal methods from many-body components of interaction-induced electric properties. The VMFC, SSFC and TB methods have been employed in order to obtain the incremental optical components for linear hydrogen fluoride clusters $(HF)_n$, where $n \in \{3, 4\}$. Following Mierzwicki and Latajka [9], who have performed similar calculations for the interaction energy, we compare these three methods of eliminating BSSE using several Dunning's correlation consistent basis sets.

The following questions are raised

- How large is the BSSE in the many-body components of interaction-induced electric properties for the analyzed cluster, especially hyperpolarizability?
- What are the differences between results obtained with various methods?
- Are the conclusions about these methods in interaction-induced electric property calculations similar to those for the interaction energy?

2 Theoretical outlook and methodology

The structures of the analyzed clusters have been incorporated from a paper published by Turi and Dannenberg [37]. As mentioned above, the linear HF trimer and tetramer are taken into account. Additional constraints have been applied as follows (see also Fig. 1):

- All monomers in N-mers have the same geometry, obtained by optimizing the isolated HF molecule at the MP2/6-31G** level o theory. The intramolecular bond length was 0.9213Å.
- All intermolecular distances between neighboring molecules in N-mers are the same and equal to 1.8618Å, which is the intermolecular separation in a linear dimer optimized at the MP2/6-31G** level of theory.
- In further calculations, N-mers are placed along the z-axis of the Cartesian coordinate system.

Since geometrical divagations are not the main interest of the present work, these assumptions were used in order to simplify the calculations.

As described below, the properties of the subsystems need to be known for SM calculations of interaction-induced properties. In the present study the finite field (FF) method [38] has been used in order to obtain static electronic dipole moment and (hyper)polarizabilities of the interacting species. This is a straightforward numerical procedure that arises directly from the definition of molecular optical properties. The energy of the isolated molecule in an external electric field $(\vec{F})$ can be expanded in a Taylor series as follows:

$$E(F) = E(0) - \sum_i \mu_i F_i - \frac{1}{2!}\sum_i \sum_j \alpha_{ij} F_i F_j - \frac{1}{3!}\sum_i \sum_j \sum_k \beta_{ijk} F_i F_j F_k - \cdots \quad (1)$$

Therefore, the coefficients: μ_i, α_{ij} and β_{ijk}, which denote molecular dipole moment, polarizability and hyperpolarizability components respectively, are identified as derivatives of the molecular energy with respect to the applied field. This leads to the FF procedure, which is simply a numerical differentiation. The method has one

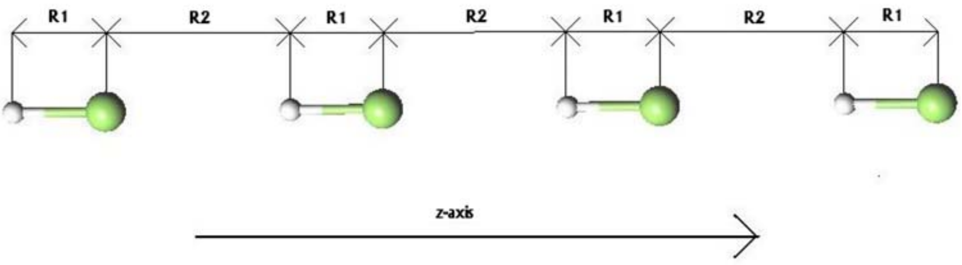

Fig. 1 Structure of the analyzed tetramer and its arrangement with respect to the coordinate system

major advantage; it can be combined with any quantum chemical method. In order to obtain electric properties, one needs only the values of the molecular energy calculated for a few field strengths. Unfortunately, the FF method also has a major drawback, namely, the results are field-dependent and care must be taken when choosing the field strength. An extensive discussion of the FF procedure can be found in a review by Kurtz and Dudis [39].

Similarly to the definition of the interaction energy, an interaction-induced property within the SM approach can be defined as the difference between the value of the property for the whole systems and its isolated constituents:

$$\Delta P_N^{\mathrm{tot}} = P_{1,2\ldots,N}(R, \xi, \Xi_1, \Xi_2, \ldots, \Xi_N) - \sum_{i=1}^{N} P_i(\Xi_i). \tag{2}$$

In the above equation Ξ_I are the internal coordinates of the interacting species, whereas R and ξ are the intermolecular separations and angles defining their mutual orientation in space. $\Delta P_N^{\mathrm{tot}}$ is the total interaction-induced property of the N-mer, which can be further decomposed into many-body components as follows:

$$\begin{aligned}\Delta P_N^{\mathrm{tot}} &= \sum_{j>i} \Delta_{ij} P^{(2)} + \sum_{k>j>i} \Delta_{ijk} P^{(3)} \\ &\quad + \cdots + \sum_{i_{N-1} > \cdots > k > j > i} \Delta_{ijk\ldots i_{N-1}} P^{(N-1)} + \Delta_{ijk\ldots N} P^{(N)}.\end{aligned} \tag{3}$$

The N-body components in the SM approach are calculated hierarchically. First, one needs to obtain the two-body terms of all possible dimers, after which the three-body components are calculated, etc. In general, an N-body component is given by:

$$\begin{aligned}\Delta_{ijk\ldots N} P^{(N)} &= \Delta P_N^{\mathrm{tot}} - \sum_{j>i} \Delta_{ij} P^{(2)} - \sum_{k>j>i} \Delta_{ijk} P^{(3)} \\ &\quad - \cdots - \sum_{i_{N-1} > \cdots > k > j > i} \Delta_{ijk\ldots i_{N-1}} P^{(N-1)}\end{aligned} \tag{4}$$

In the original Boys–Bernardi procedure, the BSSE is removed from an interaction-induced property (interaction energy) by requiring that the same (dimeric) basis set be used when calculating either the dimer or monomers:

$$\Delta P_2^{\mathrm{CP,tot}} = P_{12}(\varphi_1, \varphi_2) - P_1(\varphi_1, \varphi_2) - P_2(\varphi_1, \varphi_2), \tag{5}$$

φ_i in the brackets is the set of basis functions centered on subsystem i.

The SSFC method is a simple generalization of the Boys–Bernardi procedure. The authors assumed that analogically to the CP method for dimers, the basis set of the whole system needs to be used in the SM calculations for larger systems. Hence, in the SSFC method the total interaction-induced property of an N-mer is calculated as follows:

$$\begin{aligned}\Delta P_N^{\mathrm{SSFC,tot}} &= P_{1,2\ldots,N}(\varphi_1, \varphi_2, \ldots, \varphi_N) \\ &\quad - \sum_{i=1}^{N} P_i(\varphi_1, \varphi_2, \ldots, \varphi_N).\end{aligned} \tag{6}$$

Similarly, all two-, three- and N-body terms are calculated using the same maximal basis set:

$$\begin{aligned}\Delta_{ijk\ldots N} P^{\mathrm{SSFC},(N)}(\varphi_1, \varphi_2, \ldots, \varphi_N) &= \Delta P_N^{\mathrm{SSFC,tot}} \\ &\quad - \sum_{j>i} \Delta_{ij} P^{(2)}(\varphi_1, \varphi_2, \ldots, \varphi_N) \\ &\quad - \sum_{k>j>i} \Delta_{ijk} P^{(3)}(\varphi_1, \varphi_2, \ldots, \varphi_N) \\ &\quad - \cdots - \sum_{i_{N-1} > \cdots > k > j > i} \Delta_{ijk\ldots i_{N-1}} P^{(N-1)}(\varphi_1, \varphi_2, \ldots, \varphi_N).\end{aligned} \tag{7}$$

Different assumption is made in the VMFC method. This procedure utilizes the fact that the N-body term appears when the N-th monomer is added to the $(N-1)$-body system. Thus, this particular N-body term is calculated in the N-mer basis set, as in the SSFC approximation. All other required two-, three- $\cdots$ and $(N-1)$-body terms are obtained using the N-mer basis set as well:

$$\begin{aligned}\Delta_{ijk\ldots N} P^{\mathrm{VMFC},(N)}(\varphi_1, \varphi_2, \ldots, \varphi_N) &= \Delta P_N^{\mathrm{SSFC,tot}} \\ &\quad - \sum_{j>i} \Delta_{ij} P^{(2)}(\varphi_1, \varphi_2, \ldots, \varphi_N) \\ &\quad - \sum_{k>j>i} \Delta_{ijk} P^{(3)}(\varphi_1, \varphi_2, \ldots, \varphi_N) \\ &\quad - \cdots - \sum_{i_{N-1} > \cdots > k > j > i} \Delta_{ijk\ldots i_{N-1}} P^{(N-1)}(\varphi_1, \varphi_2, \ldots, \varphi_N).\end{aligned} \tag{8}$$

But unlike the SSFC method, the $(N-1)$-mer basis sets are used when calculating $(N-1)$-body terms:

$$\begin{aligned}\Delta_{ijk\ldots i_{N-1}} P^{\mathrm{VMFC},(N-1)}(\varphi_1, \varphi_2, \ldots, \varphi_{i_{N-1}}) &= \Delta P_{N-1}^{\mathrm{SSFC,tot}} \\ &\quad - \sum_{j>i} \Delta_{ij} P^{(2)}(\varphi_1, \varphi_2, \ldots, \varphi_{i_{N-1}}) \\ &\quad - \sum_{k>j>i} \Delta_{ijk} P^{(3)}(\varphi_1, \varphi_2, \ldots, \varphi_{i_{N-1}}) \\ &\quad - \cdots - \sum_{i_{N-2} > \cdots > k > j > i} \Delta_{ijk\ldots i_{N-2}} P^{(N-2)}(\varphi_1, \varphi_2, \ldots, \varphi_{i_{N-1}}).\end{aligned} \tag{9}$$

This leads to a hierarchical expression for the total (VMFC) interaction-induced property:

$$\begin{aligned}\Delta P_N^{\mathrm{VMFC,tot}} &= \sum_{j>i} \Delta_{ij} P^{(2)}(\varphi_i, \varphi_j) + \sum_{k>j>i} \Delta_{ijk} P^{(3)}(\varphi_i, \varphi_j, \varphi_k) \\ &\quad + \cdots + \sum_{i_{N-1} > \cdots > k > j > i} \Delta_{ijk\cdots i_{N-1}} P^{(N-1)}(\varphi_i, \varphi_j, \varphi_k, \ldots, \varphi_{i_{N-1}}) \\ &\quad + \Delta_{ijk\ldots N} P^{(N)}(\varphi_i, \varphi_j, \varphi_k, \ldots, \varphi_N).\end{aligned} \tag{10}$$

The TB method is based on the observation that $\Delta P_N^{\mathrm{tot}}$ can be decomposed into two-body terms, and all of them are calculated according to Boys–Bernardi procedure:

$$\begin{aligned}
\Delta P_N^{\mathrm{TB,tot}} &= \frac{2!(N-2)!}{N!}\sum_{j>i}\Delta_{i-j}P^{(2)}(\varphi_i,\varphi_j) \\
&+\frac{2!(N-3)!}{N!}\sum_{j>i}\sum_{\substack{k\neq i\\ k\neq j}}\Delta_{ij-k}P^{(2)}(\varphi_i,\varphi_j,\varphi_k) \\
&+\frac{3!(N-4)!}{N!}\sum_{k>j>i}\sum_{\substack{i_4\neq i\\ i_4\neq j\\ i_4\neq k}}\Delta_{ijk-i_4}P^{(2)}(\varphi_i,\varphi_j,\varphi_k,\varphi_{i_4}) \\
&+\cdots+\frac{(N-2)!1!}{N!}\sum_{i_{N-2}>\cdots>k>j>i} \\
&\times\sum_{\substack{i_{N-1}\neq i\\ i_{N-1}\neq j\\ i_{N-1}\neq k\\ \vdots\\ i_{N-1}\neq i_{N-2}}}\Delta_{ijk\ldots i_{N-2}-i_{N-1}}P^{(2)}(\varphi_i,\varphi_j,\varphi_k,\ldots,\varphi_{i_{N-2}},\varphi_{i_{N-1}}) \\
&+\frac{(N-1)!0!}{N!}\sum_{i_{N-1}>i_{N-2}>\cdots>k>j>i} \\
&\times\sum_{\substack{i_N\neq i\\ i_N\neq j\\ i_N\neq k\\ \vdots\\ i_N\neq i_{N-2}\\ i_N\neq i_{N-1}}}\Delta_{ijk\ldots i_{N-2}i_{N-1}-i_N}P^{(2)}(\varphi_i,\varphi_j,\varphi_k,\ldots,\varphi_{i_{N-2}},\varphi_{i_{N-1}},\varphi_{i_N}).
\end{aligned} \tag{11}$$

In above equation, the dash after the delta indicates the way the cluster is divided into two-body systems, i.e. *ij-k* means that the trimer *ijk* is divided into the dimer *ij* and monomer *k*. The TB method allows the N-body term to be calculated as a combination of two-body terms as follows:

$$\begin{aligned}
\Delta_{ijk\ldots N}P^{\mathrm{TB},(N)} &= 2\frac{(-1)^N}{N}\sum_{j>i}\Delta_{i-j}P^{(2)}(\varphi_i,\varphi_j) \\
&+\frac{(-1)^{N-1}}{N}\sum_{j>i}\sum_{\substack{k\neq i\\ k\neq j}}\Delta_{ij-k}P^{(2)}(\varphi_i,\varphi_j,\varphi_k) \\
&+\cdots+\frac{(-1)^2}{N}\sum_{i_{N-1}>i_{N-2}>\cdots>k>j>i} \\
&\times\sum_{\substack{i_N\neq i\\ i_N\neq j\\ i_N\neq k\\ \vdots\\ i_N\neq i_{N-2}\\ i_N\neq i_{N-1}}}\Delta_{ijk\ldots i_{N-2}i_{N-1}-i_N}P^{(2)}(\varphi_i,\varphi_j,\varphi_k,\ldots,\varphi_{i_{N-2}},\varphi_{i_{N-1}},\varphi_{i_N}).
\end{aligned} \tag{12}$$

The following dependences between the results obtained using the SSFC, VMFC and TB methods are fulfilled:

- two-body terms calculated with the VMFC and TB methods are identical,
- the *N*-body term of the *N*-mer obtained with the SSFC method is equal to that of the VMFC method.

In present work the basis set superposition error is calculated as the difference between the uncorrected and counterpoise corrected value of the interaction-induced property or its *N*-body component:

$$\mathrm{BSSE} = \Delta P^{\mathrm{UNCORR}} - \Delta P^{\mathrm{CORR}} \tag{13}$$

Most of the calculations in the present work have been performed at the FF/MP2 level of theory as implemented in the Gamess package [40] with the reference field strength of 0.001*a.u.* In order to check if conclusions could be generalized, the CCSD results have been obtained for HF trimer. Two Dunning's correlated consistent basis sets (aug-cc-pVDZ and aug-cc-pVTZ) [41–44] have been applied. For the sake of simplicity, only the longitudinal components of static electronic interaction-induced electric properties (μ_z, α_{zz} and β_{zzz}) are taken into account.

3 Results and discussion

The calculated incremental electric properties of the linear HF trimer and their two- and three-body components are presented in Tables 1 and 2.

Similarly to the results obtained for the interaction energy by Mierzwicki and Latajka [9], the total interaction-induced electric properties calculated with the TB method lie in between those computed using the SSFC and VMFC procedures. In the case of two- or three-body components, this trend is not observed.

The BSSE values estimated with various counterpoise methods for the incremental components of the molecular dipole moment and polarizability do not differ much. This is due to the fact that the results obtained with both basis sets are close to the complete basis set limit. Thus, the uncorrected interaction-induced dipole moment and polarizability are almost unaffected by the BSSE. On the contrary, the difference between the BSSE values obtained using the VMFC and SSCF methods reaches 20% in the case of the incremental first-order hyperpolarizability.

In order to compare the contribution of two- and three-body terms to the total incremental electric properties, the parameter $\Delta P^{\mathrm{rel},3/2}$ is introduced as the following ratio:

$$\Delta P^{\mathrm{rel},3/2} = \frac{\Delta_{123}P^{(3)}}{\sum_{j>i}\Delta_{ij}P^{(2)}}. \tag{14}$$

The TB method gives the highest values of $\Delta P^{\mathrm{rel},3/2}$ in comparison with all three counterpoise methods. On the contrary the uncorrected method underestimates the contribution of three-body terms. This is visible in the case

Table 1 The two- and three-body components of interaction-induced electric properties for the hydrogen fluoride trimer, calculated with various counterpoise procedures at the MP2/aug-cc-pVDZ level of theory

	UNCORR	SSFC	VMFC	TB	BSSE (SSFC)	BSSE (VMFC)	BSSE (TB)
Incremental dipole moment, $\Delta\mu_z$ (*a.u.*)							
$\Sigma\Delta_{ij}\mu_z^{(2)}$	−0.3657	−0.3640	−0.3639	−0.3639	−0.0017	−0.0018	−0.0018
1-2	−0.1746	−0.1740	−0.1739	−0.1739	−0.0006	−0.0007	−0.0007
1-3	−0.0164	−0.0163	−0.0160	−0.0160	−0.0001	−0.0004	−0.0004
2-3	−0.1746	−0.1737	−0.1739	−0.1739	−0.0009	−0.0007	−0.0007
$\Delta_{123}\mu_z^{(3)}$	−0.0166	−0.0170	−0.0170	−0.0171	0.0004	0.0004	0.0005
$\Delta\mu_z^{\mathrm{rel},3/2}$	0.045	0.047	0.047	0.047			
$\Delta\mu_{z,123}^{\mathrm{int}}$	−0.3823	−0.3810	−0.3808	−0.3809	−0.0013	−0.0014	−0.0014
Incremental polarizability, $\Delta\alpha_{zz}$ (*a.u.*)							
$\Sigma\Delta_{ij}\alpha_{zz}^{(2)}$	2.18	2.04	2.03	2.03	0.13	0.15	0.15
1-2	1.04	0.96	0.96	0.96	0.07	0.08	0.08
1-3	0.10	0.12	0.11	0.11	−0.02	−0.01	−0.01
2-3	1.04	0.95	0.96	0.96	0.08	0.08	0.08
$\Delta_{123}\alpha_{zz}^{(3)}$	0.16	0.14	0.14	0.15	0.02	0.02	0.01
$\Delta\alpha_{zz}^{\mathrm{rel},3/2}$	0.073	0.067	0.068	0.073			
$\Delta\alpha_{zz,123}^{\mathrm{int}}$	2.34	2.18	2.17	2.18	0.16	0.17	0.16
Incremental hyperpolarizability, $\Delta\beta_{zzz}$ (*a.u.*)							
$\Sigma\Delta_{ij}\beta_{zzz}^{(2)}$	−10.9	−8.0	−7.2	−7.2	−3.0	−3.7	−3.7
1-2	−5.6	−3.8	−3.6	−3.6	−1.8	−2.0	−2.0
1-3	0.3	−0.1	0.1	0.1	0.4	0.2	0.2
2-3	−5.6	−4.0	−3.6	−3.6	−1.6	−2.0	−2.0
$\Delta_{123}\beta_{zzz}^{(3)}$	−6.3	−5.2	−5.2	−5.7	−1.0	−1.0	−0.5
$\Delta\beta_{zzz}^{\mathrm{rel},3/2}$	0.57	0.66	0.73	0.80			
$\Delta\beta_{zzz,123}^{\mathrm{int}}$	−17.2	−13.2	−12.4	−12.9	−4.0	−4.8	−4.3

Table 2 The two- and three-body components of interaction-induced electric properties for the hydrogen fluoride trimer, calculated with various counterpoise procedures at the MP2/aug-cc-pVTZ level of theory

	UNCORR	SSFC	VMFC	TB	BSSE (SSFC)	BSSE (VMFC)	BSSE (TB)
Incremental dipole moment, $\Delta\mu_z$ (*a.u.*)							
$\Sigma\Delta_{ij}\mu_z^{(2)}$	−0.3672	−0.3677	−0.3676	−0.3676	0.0005	0.0004	0.0004
1-2	−0.1754	−0.1756	−0.1756	−0.1756	0.0002	0.0002	0.0002
1-3	−0.0164	−0.0165	−0.0164	−0.0164	0.0001	0.0000	0.0000
2-3	−0.1754	−0.1756	−0.1756	−0.1756	0.0002	0.0002	0.0002
$\Delta_{123}\mu_z^{(3)}$	−0.0176	−0.0174	−0.0174	−0.0175	−0.0002	−0.0002	−0.0001
$\Delta\mu_z^{\mathrm{rel},3/2}$	0.048	0.047	0.047	0.048			
$\Delta\mu_{z,123}^{\mathrm{int}}$	−0.3848	−0.3851	−0.3850	−0.3851	0.0003	0.0002	0.0002
Incremental polarizability, $\Delta\alpha_{zz}$ (*a.u.*)							
$\Sigma\Delta_{ij}\alpha_{zz}^{(2)}$	2.16	2.11	2.09	2.09	0.05	0.07	0.07
1-2	1.02	0.99	0.99	0.99	0.03	0.04	0.04
1-3	0.12	0.13	0.12	0.12	−0.01	0.00	0.00
2-3	1.02	0.99	0.99	0.99	0.03	0.04	0.04
$\Delta_{123}\alpha_{zz}^{(3)}$	0.16	0.14	0.14	0.15	0.02	0.02	0.01
$\Delta\alpha_{zz}^{\mathrm{rel},3/2}$	0.072	0.065	0.065	0.071			
$\Delta\alpha_{zz,123}^{\mathrm{int}}$	2.32	2.25	2.23	2.24	0.07	0.09	0.08
Incremental hyperpolarizability, $\Delta\beta_{zzz}$ (*a.u.*)							
$\Sigma\Delta_{ij}\beta_{zzz}^{(2)}$	−11.0	−8.1	−7.3	−7.3	−2.9	−3.7	−3.7
1-2	−5.5	−4.1	−3.6	−3.6	−1.4	−1.8	−1.8
1-3	0.0	−0.1	0.0	0.0	0.1	0.0	0.0
2-3	−5.5	−4.0	−3.6	−3.6	−1.5	−1.8	−1.8
$\Delta_{123}\beta_{zzz}^{(3)}$	−5.7	−5.0	−5.0	−5.5	−0.8	−0.8	−0.2
$\Delta\beta_{zzz}^{\mathrm{rel},3/2}$	0.52	0.61	0.68	0.75			
$\Delta\beta_{zzz,123}^{\mathrm{int}}$	−16.7	−13.1	−12.2	−12.8	−3.6	−4.5	−3.9

Table 3 The two- and many-body components of interaction-induced electric properties for the HF tetramer, calculated with various counterpoise procedures at the MP2/aug-cc-pVDZ level of theory

	UNCORR	SSFC	VMFC	TB	BSSE (SSFC)	BSSE (VMFC)	BSSE (TB)
Incremental dipole moment, $\Delta\mu_z$ (*a.u.*)							
$\Sigma\Delta_{ij}\mu_z^{(2)}$	−0.5614	−0.5589	−0.5584	−0.5584	−0.0025	−0.0030	−0.0030
1-2	−0.1746	−0.1740	−0.1739	−0.1739	−0.0006	−0.0007	−0.0007
1-3	−0.0164	−0.0164	−0.0160	−0.0160	−0.0001	−0.0004	−0.0004
1-4	−0.0046	−0.0047	−0.0046	−0.0046	0.0000	0.0000	0.0000
2-3	−0.1746	−0.1738	−0.1739	−0.1739	−0.0008	−0.0007	−0.0007
2-4	−0.0164	−0.0163	−0.0160	−0.0160	−0.0001	−0.0004	−0.0004
3-4	−0.1746	−0.1737	−0.1739	−0.1739	−0.0009	−0.0007	−0.0007
$\Sigma\Delta_{ijk}\mu_z^{(3)}$	−0.0374	−0.0380	−0.0379	−0.0382	0.0006	0.0006	0.0008
1-2-3	−0.0166	−0.0170	−0.0170	−0.0171	0.0004	0.0004	0.0005
2-3-4	−0.0166	−0.0170	−0.0170	−0.0171	0.0004	0.0004	0.0005
1-2-4	−0.0021	−0.0021	−0.0021	−0.0021	0.0000	0.0000	0.0001
1-3-4	−0.0021	−0.0019	−0.0019	−0.0019	−0.0002	−0.0002	−0.0002
$\Delta\mu_z^{\mathrm{rel},3/2}$	0.07	0.07	0.07	0.07			
$\Delta_{1234}\mu_z^{(4)}$	−0.0018	−0.0016	−0.0016	−0.0017	−0.0002	−0.0002	−0.0001
$\Delta\mu_z^{\mathrm{rel},4/2}$	0.003	0.003	0.003	0.003			
$\Delta\mu_{z,1234}^{\mathrm{int}}$	−0.6005	−0.5985	−0.5980	−0.5983	−0.0020	−0.0025	−0.0022
Incremental polarizability, $\Delta\alpha_{zz}$ (*a.u.*)							
$\Sigma\Delta_{ij}\alpha_{zz}^{(2)}$	3.35	3.16	3.13	3.13	0.19	0.22	0.22
1-2	1.04	0.96	0.96	0.96	0.08	0.08	0.08
1-3	0.10	0.13	0.11	0.11	−0.03	−0.01	−0.01
1-4	0.03	0.04	0.03	0.03	0.00	0.00	0.00
2-3	1.04	0.96	0.96	0.96	0.08	0.08	0.08
2-4	0.10	0.12	0.11	0.11	−0.02	−0.01	−0.01
3-4	1.04	0.96	0.96	0.96	0.08	0.08	0.08
$\Sigma\Delta_{ijk}\alpha_{zz}^{(3)}$	0.36	0.30	0.30	0.32	0.07	0.06	0.04
1-2-3	0.16	0.14	0.14	0.15	0.02	0.02	0.01
2-3-4	0.16	0.14	0.14	0.15	0.02	0.02	0.01
1-2-4	0.02	0.02	0.02	0.02	0.00	0.00	0.00
1-3-4	0.03	0.01	0.01	0.01	0.02	0.01	0.01
$\Delta\alpha_{zz}^{\mathrm{rel},3/2}$	0.11	0.09	0.10	0.10			
$\Delta_{1234}\alpha_{zz}^{(4)}$	0.01	0.03	0.03	0.03	−0.02	−0.02	−0.01
$\Delta\alpha_{zz}^{\mathrm{rel},4/2}$	0.00	0.01	0.01	0.01			
$\Delta\alpha_{zz,1234}^{\mathrm{int}}$	3.73	3.49	3.47	3.48	0.24	0.26	0.24
Incremental hyperpolarizability, $\Delta\beta_{zzz}$ [*a.u.*]							
$\Sigma\Delta_{ij}\beta_{zzz}^{(2)}$	−16.2	−12.6	−10.7	−10.7	−3.7	−5.5	−5.5
1-2	−5.6	−4.0	−3.6	−3.6	−1.6	−2.0	−2.0
1-3	0.3	−0.1	0.1	0.1	0.4	0.2	0.2
1-4	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2-3	−5.6	−4.3	−3.6	−3.6	−1.3	−2.0	−2.0
2-4	0.3	−0.1	0.1	0.1	0.4	0.2	0.2
3-4	−5.6	−4.0	−3.6	−3.6	−1.6	−2.0	−2.0
$\Sigma\Delta_{ijk}\beta_{zzz}^{(3)}$	−14.8	−12.3	−12.7	−13.7	−2.5	−2.1	−1.1
1-2-3	−6.3	−5.0	−5.2	−5.7	−1.2	−1.0	−0.5
2-3-4	−6.3	−5.1	−5.2	−5.7	−1.2	−1.0	−0.5
1-2-4	−1.3	−1.3	−1.3	−1.3	0.0	0.0	0.0
1-3-4	−1.0	−0.9	−0.9	−0.9	−0.1	−0.1	−0.1
$\Delta\beta_{zzz}^{\mathrm{rel},3/2}$	0.91	0.98	1.19	1.28			

Table 3 continued

	UNCORR	SSFC	VMFC	TB	BSSE (SSFC)	BSSE (VMFC)	BSSE (TB)
$\Delta_{1234}\beta^{(4)}_{zzz}$	1.5	1.3	1.3	1.4	0.2	0.2	0.1
$\Delta\beta^{\mathrm{rel},4/2}_{zzz}$	−0.10	−0.11	−0.12	−0.13			
$\Delta\beta^{\mathrm{int}}_{zzz,1234}$	−29.5	−23.5	−22.0	−23.0	−5.9	−7.4	−6.5

Table 4 The two- and many-body components of interaction-induced electric properties for the HF tetramer, calculated with various counterpoise procedures at the MP2/aug-cc-pVTZ level of theory

	UNCORR	SSFC	VMFC	TB	BSSE (SSFC)	BSSE (VMFC)	BSSE (TB)
Incremental dipole moment, $\Delta\mu_z$ (*a.u.*)							
$\Sigma\Delta_{ij}\mu^{(2)}_z$	−0.5637	−0.5646	−0.5643	−0.5643	0.0008	0.0005	0.0005
1-2	−0.1754	−0.1756	−0.1756	−0.1756	0.0002	0.0002	0.0002
1-3	−0.0164	−0.0165	−0.0164	−0.0164	0.0001	0.0000	0.0000
1-4	−0.0047	−0.0048	−0.0047	−0.0047	0.0000	0.0000	0.0000
2-3	−0.1754	−0.1756	−0.1756	−0.1756	0.0002	0.0002	0.0002
2-4	−0.0164	−0.0165	−0.0164	−0.0164	0.0001	0.0000	0.0000
3-4	−0.1754	−0.1756	−0.1756	−0.1756	0.0002	0.0002	0.0002
$\Sigma\Delta_{ijk}\mu^{(3)}_z$	−0.0393	−0.0390	−0.0389	−0.0391	−0.0004	−0.0004	−0.0002
1-2-3	−0.0176	−0.0174	−0.0174	−0.0175	−0.0002	−0.0002	−0.0001
2-3-4	−0.0176	−0.0174	−0.0174	−0.0175	−0.0002	−0.0002	−0.0001
1-2-4	−0.0022	−0.0022	−0.0021	−0.0022	0.0000	0.0000	0.0000
1-3-4	−0.0019	−0.0020	−0.0020	−0.0020	0.0000	0.0000	0.0000
$\Delta\mu^{\mathrm{rel},3/2}_z$	0.07	0.07	0.07	0.07			
$\Delta_{1234}\mu^{(4)}_z$	−0.0018	−0.0017	−0.0017	−0.0017	−0.0001	−0.0001	0.0000
$\Delta\mu^{\mathrm{rel},4/2}_z$	0.003	0.003	0.003	0.003			
$\Delta\mu^{\mathrm{int}}_{z,1234}$	−0.6049	−0.6052	−0.6049	−0.6051	0.0004	0.0000	0.0002
Incremental polarizability, $\Delta\alpha_{zz}$ (*a.u.*)							
$\Sigma\Delta_{ij}\alpha^{(2)}_{zz}$	3.33	3.27	3.23	3.23	0.07	0.10	0.10
1-2	1.02	0.99	0.99	0.99	0.03	0.04	0.04
1-3	0.12	0.13	0.12	0.12	−0.01	0.00	0.00
1-4	0.03	0.04	0.03	0.03	0.00	0.00	0.00
2-3	1.02	0.99	0.99	0.99	0.03	0.04	0.04
2-4	0.12	0.13	0.12	0.12	−0.01	0.00	0.00
3-4	1.02	0.99	0.99	0.99	0.03	0.04	0.04
$\Sigma\Delta_{ijk}\alpha^{(3)}_{zz}$	0.35	0.31	0.30	0.33	0.04	0.04	0.02
1-2-3	0.16	0.14	0.14	0.15	0.02	0.02	0.01
2-3-4	0.16	0.14	0.14	0.15	0.02	0.02	0.01
1-2-4	0.02	0.02	0.02	0.02	0.00	0.00	0.00
1-3-4	0.02	0.01	0.01	0.01	0.00	0.00	0.00
$\Delta\alpha^{\mathrm{rel},3/2}_{zz}$	0.10	0.09	0.09	0.10			
$\Delta_{1234}\alpha^{(4)}_{zz}$	0.03	0.03	0.03	0.03	0.00	0.00	0.00
$\Delta\alpha^{\mathrm{rel},4/2}_{zz}$	0.01	0.01	0.01	0.01			
$\Delta\alpha^{\mathrm{int}}_{zz,1234}$	3.71	3.61	3.57	3.59	0.11	0.14	0.12
Incremental hyperpolarizability, $\Delta\beta_{zzz}$ (*a.u.*)							
$\Sigma\Delta_{ij}\beta^{(2)}_{zzz}$	−16.4	−11.9	−10.8	−10.8	−4.5	−5.5	−5.5
1-2	−5.5	−4.0	−3.6	−3.6	−1.5	−1.8	−1.8
1-3	0.0	−0.1	0.0	0.0	0.1	0.0	0.0
1-4	0.1	0.1	0.1	0.1	0.0	0.0	0.0
2-3	−5.5	−4.1	−3.6	−3.6	−1.4	−1.8	−1.8

Table 4 continued

	UNCORR	SSFC	VMFC	TB	BSSE (SSFC)	BSSE (VMFC)	BSSE (TB)
2-4	0.0	0.0	0.0	0.0	0.1	0.0	0.0
3-4	−5.5	−3.8	−3.6	−3.6	−1.7	−1.8	−1.8
$\Sigma\Delta_{ijk}\beta_{zzz}^{(3)}$	−13.7	−13.1	−12.5	−13.3	−0.6	−1.3	−0.5
1-2-3	−5.7	−5.3	−5.0	−5.5	−0.4	−0.8	−0.2
2-3-4	−5.7	−5.2	−5.0	−5.5	−0.6	−0.8	−0.2
1-2-4	−1.3	−1.6	−1.3	−1.3	0.3	0.0	−0.1
1-3-4	−1.0	−1.0	−1.3	−1.0	0.0	0.3	0.0
$\Delta\beta_{zzz}^{\mathrm{rel},3/2}$	0.84	1.11	1.15	1.23			
$\Delta_{1234}\beta_{zzz}^{(4)}$	1.3	1.6	1.6	1.2	−0.3	−0.3	0.1
$\Delta\beta_{zzz}^{\mathrm{rel},4/2}$	−0.08	−0.14	−0.15	−0.11			
$\Delta\beta_{zzz,1234}^{\mathrm{int}}$	−28.8	−23.4	−21.7	−22.9	−5.4	−7.1	−5.9

Table 5 The two- and three-body components of interaction-induced electric properties for the hydrogen fluoride trimer, calculated with various counterpoise procedures at the CCSD/aug-cc-pVDZ level of theory

	UNCORR	SSFC	VMFC	TB	BSSE (SSFC)	BSSE (VMFC)	BSSE (TB)
Incremental dipole moment, $\Delta\mu_z$ (*a.u.*)							
$\Sigma\Delta_{ij}\mu_z^{(2)}$	−0.3614	−0.3600	−0.3595	−0.3595	−0.0013	−0.0019	−0.0019
1-2	−0.1726	−0.1720	−0.1719	−0.1719	−0.0006	−0.0007	−0.0007
1-3	−0.0161	−0.0160	−0.0157	−0.0157	−0.0001	−0.0004	−0.0004
2-3	−0.1726	−0.1720	−0.1719	−0.1719	−0.0006	−0.0007	−0.0007
$\Delta_{123}\mu_z^{(3)}$	−0.0162	−0.0166	−0.0166	−0.0167	0.0003	0.0003	0.0004
$\Delta\mu_z^{\mathrm{rel},3/2}$	0.045	0.046	0.046	0.046			
$\Delta\mu_{z,123}^{\mathrm{int}}$	−0.3776	−0.3762	−0.3761	−0.3762	−0.0014	−0.0015	−0.0014
Incremental polarizability, $\Delta\alpha_{zz}$ (*a.u.*)							
$\Sigma\Delta_{ij}\alpha_{zz}^{(2)}$	2.13	2.01	1.99	1.99	0.12	0.14	0.14
1-2	1.01	0.94	0.94	0.94	0.07	0.07	0.07
1-3	0.10	0.12	0.11	0.11	−0.02	−0.01	−0.01
2-3	1.01	0.94	0.94	0.94	0.07	0.07	0.07
$\Delta_{123}\alpha_{zz}^{(3)}$	0.16	0.13	0.13	0.14	0.02	0.02	0.01
$\Delta\alpha_{zz}^{\mathrm{rel},3/2}$	0.073	0.066	0.067	0.072			
$\Delta\alpha_{zz,123}^{\mathrm{int}}$	2.28	2.14	2.12	2.13	0.15	0.16	0.15
Incremental hyperpolarizability, $\Delta\beta_{zzz}$ (*a.u.*)							
$\Sigma\Delta_{ij}\beta_{zzz}^{(2)}$	−12.3	−9.5	−8.6	−8.6	−2.8	−3.7	−3.7
1-2	−6.3	−4.6	−4.3	−4.3	−1.7	−1.9	−1.9
1-3	0.2	−0.4	0.0	0.0	0.6	0.2	0.2
2-3	−6.3	−4.6	−4.3	−4.3	−1.7	−1.9	−1.9
$\Delta_{123}\beta_{zzz}^{(3)}$	−4.3	−3.2	−3.2	−3.8	−1.1	−1.1	−0.5
$\Delta\beta_{zzz}^{\mathrm{rel},3/2}$	0.35	0.34	0.38	0.44			
$\Delta\beta_{zzz,123}^{\mathrm{int}}$	−16.6	−12.8	−11.9	−12.5	−3.9	−4.7	−4.2

of the first-order hyperpolarizability, where the BSSE is far from negligible.

The three-body terms of all calculated interaction-induced electric properties for the considered trimer are cooperative, since they have the same sign as the sum of their two-body analogs ($\Delta P^{\mathrm{rel},3/2} > 0$). A large nonadditivity exists in the case of the incremental first-order hyperpolarizability. The contribution of three-body terms in $\Delta\beta_{zzz}^{\mathrm{tot}}$ reaches a dozen percent, even when calculated without the counterpoise correction. These results are in agreement with our previous calculations [32].

In Tables 3 and 4 the results of N-body decomposition of interaction-induced electric properties for the linear fluorohydrogen tetramer are gathered.

In this case, the parameters $\Delta P^{\mathrm{rel},3/2}$ and $\Delta P^{\mathrm{rel},4/2}$ are defined in a similar way as for the trimer:

$$\Delta P^{\mathrm{rel},3/2} = \frac{\sum_{k>j>i} \Delta_{ijk} P^{(3)}}{\sum_{j>i} \Delta_{ij} P^{(2)}}, \qquad (15)$$

$$\Delta P^{\mathrm{rel},4/2} = \frac{\Delta_{1234} P^{(4)}}{\sum_{j>i} \Delta_{ij} P^{(2)}}. \qquad (16)$$

The three- and four-body components of the incremental dipole moment and polarizability are cooperative in the case of the interaction-induced first-order hyperpolarizability, which has a noncooperative four-body component ($\Delta P^{\mathrm{rel},4/2} < 0$).

The dependences between the BSSE values obtained with different counterpoise schemes for the tetramer are the same as for the trimer.

In order to check if the above observations are also true for other quantum chemical methods, additional calculations have been performed at the CCSD level. In Table 5, results for CCSD/aug-cc-pVDZ calculations of interaction-induced properties and their many-body components in the HF trimer are gathered.

These data imply that the relations between BSSE obtained with the various counterpoise schemes stay unchanged. If one compares the values calculated at the MP2 and CCSD levels of theory, one can conclude that they are shifted on the scale of dipole moment or (hyper)polarizability, and that the relations between the magnitudes of BSSE remain the same.

4 Conclusions

Three counterpoise methods that remove BSSE have been applied for the first time in calculations of many-body components of interaction-induced optical properties for the linear hydrogen fluoride trimer and tetramer. BSSE values obtained using the SSFC, VMFC and TB methods converge to the same value if a saturated basis set is used (in the case of dipole moment and polarizability). In such a situation, the uncorrected values of incremental optical properties are almost unaffected by BSSE. On the other hand, if the calculated results are far from the complete basis set limit (as is the case for first-order hyperpolarizability), there are non-negligible quantitative differences between values obtained with various counterpoise methods. Since it is difficult to decide which of the analyzed procedures gives correct results, the conclusion that a saturated basis set should be applied instead of counterpoise schemes is supported. Similar unpublished calculations were performed for hydrogen cyanide, which lead to similar conclusions.

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