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Basis Set Superposition Effects on Properties of Interacting Systems. Dipole Moments and Polarizabilities

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Basis set superposition effects which are not removed by the counterpoise correction are shown to modify the electric properties of interacting subsystems and influence indirectly the calculated interaction energies. The role of these higher-order basis set superposition effects is illustrated by the calculation of the water molecule dipole moment and polarizability in the basis set of the water dimer.

Key word: Basis set superposition effect – Molecular properties – Molecular interactions.

1. Introduction

It is already well established [1] that the small basis set results for intermolecular interaction energies need to be corrected for what is known as the basis set superposition error (BSEE) [1, 2]. This can be achieved by using the counterpoise (CP) correction method [2] which removes the unwanted improvement of the subsystem energies arising from the superposition of the subsystem truncated basis sets [1, 2]. It is believed that the CP correction accounts for the major part of the basis set superposition effects.

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According to recent SCF results of Kołos [1] the BSSE corrected interaction energies calculated with optimized minimal basis sets are comparable to those obtained with much larger bases [1, 3]. This is partly due to the use of the CP correction method and partly due to the basis set optimization. The optimized minimal basis sets of Kołos give reasonable estimates of the first-order electrostatic interaction energy [1] which in most cases makes a dominant contribution to the total interaction energy. However, these minimal basis sets are not likely to describe properly the subsystem polarization [4]. Hence, the induction contribution to the interaction energy should be severely underestimated. In the light of the interpretation of the basis set superposition effects proposed by Groen and van Duijneveldt [5] and discussed in Kołos' paper [1], the closeness of the CP corrected minimal basis set results and the large basis set interaction energies [1, 3] appears to be quite puzzling.

Though the CP correction is definitely important, its effect is mostly concerned with the subsystem energies. The basis set superposition affects also the electric properties (multipole moments and polarizabilities) of each subsytem and indirectly influences the calculated interaction energy. This can be regarded as the higher-order basis set superposition effect. Its role and importance certainly deserves a careful examination. It should be pointed out that in contrast to the part of the BSSE which is removed by the CP correction, the higher-order superposition effects may contribute to the improvement of the calculated interaction energy. Some insight into their importance can be gained by the study of the basis set superposition effects on the subsystem electric moments and polarizabilities.

2. The Higher-Order Basis Set Superposition Effects

The CP corrected SCF energy of interaction between two subsystems A and B can be written as [1, 2]:

$$E_{\text{int}} = E_{AB} - E_A - E_B \tag{1}$$

where E_{AB} is the composite $(A+B)$ system SCF energy calculated in the superposed basis set $\{A\}+\{B\}=\{A+B\}$ and

$$E_i = \varepsilon_i + \Delta_i \tag{2}$$

is the ith subsystem $(i = A, B)$ SCF energy obtained in the $\{A+B\}$ basis set. ε_i denotes the i-th subsystem SCF energy computed in its own basis set $\{i\}$ and Δ_i is the corresponding CP correction. According to Groen and van Duijneveldt [5] the CP corrected SCF interaction energy can be expressed as [1]:

$$E_{\text{int}} = \Delta E^{(1)}_{AB} + \Delta E^{(2)}_{AB} \tag{3}$$

where $\Delta E^{(1)}_{AB}$ is the first-order SCF interaction energy and $\Delta E^{(2)}_{AB}$ represents all additional contributions from the SCF iterations excluding the CP terms that are accounted for by Eq. (2) [1].

For polar interacting species at long and intermediate distances R_{AB} the exchange contribution [6] to the total interaction energy (3) is presumably much smaller than the contributions due to classical electrostatic and induction interactions. Hence, the first-order electrostatic energy $\Delta E^{(1)}_{AB,\mathrm{elst}}$ and the second-order induction energy $\Delta E^{(2)}_{AB,\mathrm{ind}}$ should give the dominant part of Eq. (3). On interpreting these components of the SCF interaction energy in terms of the multipole expansion [7] one finds that the superposition of the subsystem basis sets must affect both of them; both the moments of the electron density distribution and the subsystem polarizabilities may undergo considerable changes when passing from the isolated subsystem to the supermolecule basis set. This effect is not accounted for by the CP correction.

The subsystem energy lowering which is removed by the CP method represents certainly the unwanted artifact of the truncated basis set calculations of interaction energies. However, as already pointed out, the higher-order basis set superposition effects should not necessarily be considered as the erratic contributions to E_{int}. On the contrary, they may even improve the calculated values of E_{int} via the improvement of the subsystem electric properties. In this context it is worth while to mention that the moments of the electron density distribution can be either increased or decreased by the basis set superposition. On the other hand, the superposition of the basis set functions is likely to increase the diagonal components of the polarizability tensors for each of the interacting subsystems.[1] Since the small basis set calculations of molecular polarizabilities are far from being realistic [4], increasing the basis set size via the superposition of the subsystem basis sets may result in a substantial increase of the subsystem polarizabilities. Owing to this effect the basis set superposition may considerably affect the induction energy: the induction contribution to Eq. (3) will be different from the induction energy that could have been obtained directly from the electric properties of isolated subsystems, i.e., the multipole moments and polarizabilities computed in the truncated basis set of a given subsystem.

The higher-order basis set superposition effects on the SCF interaction energy can be indirectly analysed and estimated by the calculation of the basis set superposition effect on electric properties of separate subsystems. In the next section this effect is investigated for the dipole moment and dipole polarizability of the water molecule in the water dimer minimal basis set [1].

3. Dipole Moment and Polarizability of the Water Molecule in the Water Dimer Minimal Basis Set

The supermolecule (dimer) basis employed in the present study is the minimal basis set reported by Kołos [1] and corresponds to the dimer configurations referred to as *B* and *D* in the paper by Matsuoka et al. [3]. For the sake of

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[1] The polarizability tensor diagonal components would precisely increase only if the occupied SCF orbitals of the subsystem were the exact solutions of the corresponding HF equations. For the truncated basis set SCF orbitals some decrease of the diagonal components of the polarizability tensor may also happen.

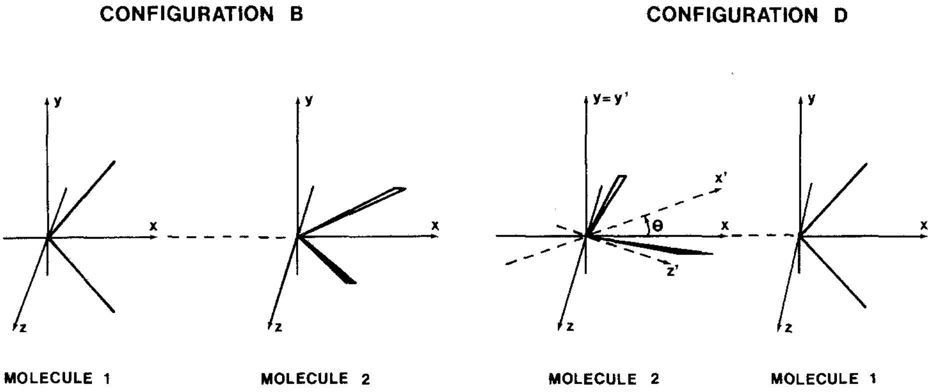

Fig. 1. The water dimer configurations *B* and *D*. In both configurations Molecule 1 lies in the *xy* plane and its C_2 symmetry axis coincides with the *x* axis of the coordinate system. Molecule 2 lies in the *xz* plane and θ is the angle between its C_2 symmetry axis (x' in the local coordinate system) and the *x* axis of the common coordinate system. For configuration *B* the angle θ equals zero

convenience the two dimer configurations are shown in Fig. 1. The monomer geometry parameters as well as the orbital origin coordinates for the dimer basis set are the same as those given by Matsuoka et al [3].

It is obvious that the basis set superposition effects for the two positions of the water molecule with respect to the dimer basis are different. Hence, the monomer dipole moment and polarizability tensor components have been computed separately for each of the two non-equivalent positions of the water molecule which are hereafter referred to as Molecule 1 and Molecule 2 (see Fig. 1). The coordinate systems employed to define the dipole moment and polarizability components are also shown in Fig. 1.

The polarizability tensor calculations have been performed by using the finite field perturbation approach [8] and follow from the straightforward numerical differentiation of the induced dipole moments with respect to the external field strength. In all calculations reported in this paper the external electric field strength for each non-equivalent direction has been chosen as equal to ±0.005 a.u.

The dipole moment and polarizability results for different O · · · O distances in configurations *B* and *D* are presented in Tables 1 and 2, respectively. The data for Molecule 2 in configuration *D* calculated in the dimer coordinate system require some additional comments. Their irregular character arises due to different angular positions of the water molecule at different O · · · O distances. However, on transforming the polarizability tensor to the local molecule-fixed coordinate system this apparent irregularity completely disappears. For this reason the corresponding data have been given for both the dimer-fixed and the molecule-fixed coordinate system (Fig. 1).

The minimal basis set value of the dipole moment for the isolated water molecule (0.880 a.u.) is not too far from the near-HF result (0.782 a.u. [9]). This is mainly

Table 1. Dipole moment and polarizability of the water molecule in the water dimer minimal basis set: configuration B.[a] All entries in a.u.

$R_{00}=$	∞	15.0	11.0	9.0	8.0	7.0	6.0	5.5	5.0	4.5
Molecule 1[b]										
μ_x	0.880	0.880	0.880	0.880	0.880	0.880	0.879	0.878	0.876	0.873
α_{xx}	2.74	2.74	2.74	2.74	2.75	2.75	2.79	2.84	2.93	3.07
α_{yy}	6.84	6.85	6.85	6.85	6.85	6.85	6.85	6.85	6.85	6.85
α_{zz}	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.03	0.03	0.05
Molecule 2[b]										
μ_x	0.880	0.880	0.880	0.880	0.880	0.883	0.897	0.914	0.940	0.971
α_{xx}	2.74	2.74	2.75	2.75	2.75	2.80	3.00	3.23	3.54	3.92
α_{yy}	0.02	0.02	0.02	0.02	0.02	0.03	0.05	0.06	0.11	0.19
α_{zz}	6.84	6.85	6.85	6.85	6.84	6.84	6.81	6.82	6.80	6.78

[a] The details concerning the dimer geometry, coordinate systems and notation are explained in Fig. 1. See also Ref. [3].

[b] All components are defined with respect to the dimer-fixed coordinate systems. See Fig. 1.

Table 2. Dipole moment and polarizability of the water molecule in the water dimer minimal basis set: configuration D.[a] Distances, dipole moments and polarizabilities in a.u.

$R_{00}=$	15.0	11.0	9.0	8.0	7.0	6.0	5.5	5.0	4.5
$\theta=$	0.00°	30.94°	39.96°	43.41°	−46.16°	47.95°	−47.98°	−34.18°	0.00°
Molecule 1[b]									
μ_x	0.880	0.880	0.880	0.881	0.888	0.913	0.934	0.950	0.971
μ_z	0.000	0.000	0.000	0.000	0.000	0.001	−0.002	−0.008	0.000
α_{xx}	2.74	2.74	2.75	2.77	2.86	3.19	3.45	3.69	3.92
α_{xz}	0.00	0.00	0.00	0.00	0.00	0.01	−0.02	−0.10	0.00
α_{yy}	6.84	6.85	6.85	6.85	6.80	6.81	6.81	6.80	6.78
α_{zz}	0.02	0.02	0.02	0.02	0.02	0.03	0.03	0.06	0.19
Molecule 2[b]									
μ_x	0.880	0.755	0.674	0.639	0.610	0.593	0.596	0.734	0.873
μ_z	0.000	0.452	0.565	0.604	−0.635	0.653	−0.654	−0.496	0.000
α_{xx}	2.75	3.83	4.44	4.69	4.89	5.06	5.09	4.20	3.07
α_{xz}	0.00	−1.81	−2.02	−2.05	2.05	−2.04	2.04	1.88	0.00
α_{yy}	0.02	0.02	0.02	0.02	0.02	0.03	0.03	0.04	0.05
α_{zz}	6.85	5.76	5.16	4.91	4.71	4.59	4.59	5.56	6.85
Molecule 2[c]									
$\mu_{x'}$	0.880	0.880	0.880	0.880	0.880	0.882	0.884	0.886	0.873
$\mu_{z'}$	0.000	0.000	0.000	0.000	0.000	−0.003	0.005	0.003	0.000
$\alpha_{x'x'}$	2.75	2.75	2.75	2.75	2.75	2.77	2.79	2.88	3.07
$\alpha_{x'z'}$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	−0.01	0.00
$\alpha_{y'y'}$	0.02	0.02	0.02	0.02	0.02	0.03	0.03	0.04	0.05
$\alpha_{z'z'}$	6.85	6.85	6.85	6.85	6.85	6.88	6.89	6.88	6.85

[a] For the details concerning the dimer geometry, coordinate systems and symbols see Fig. 1 and Ref. [3].

[b] Components defined with respect to the dimer-fixed coordinate system. See Fig. 1.

[c] Components defined with respect to the local coordinate system of Molecule 2. The angle between the $x-$ and x'-axis is denoted by θ. See Fig. 1.

due to the basis set optimization [1]. However, it can be seen from the data of Table 1 that the isolated molecule polarizability components are obviously much too low. In the coordinate system of Molecule 1 the minimal basis set results for the diagonal components of the polarizability tensor α_{xx}, α_{yy}, and α_{zz} are 2.74, 6.84, and 0.01 a.u., repectively. They are much lower than the corresponding near-HF values (8.47, 9.04, and 7.99 a.u. in the same coordinate system as above [9]). Hence, the inaccuracy of the minimal basis set result for the dipole moment will lead to some overestimation of the dipole–dipole electrostatic interaction energy, while the use of the minimal basis set data for polarizabilities results in underestimating the long-range dipole–induced–dipole interaction.

It follows from the data of Tables 1 and 2 that in both configurations of the dimer the basis set superposition results in a considerable increase of the x component of the dipole moment and the xx component of the polarizability tensor for the water molecule which plays the role of the electron pair donor in the dimer. For the other molecule the μ_x value is only slightly affected by the basis set superposition. Also the increase of α_{xx} is much smaller than for the electron pair donor molecule. Thus, one can expect that the basis set superposition effects should lead to the enhancement of both the dipole–dipole and dipole–induced–dipole interaction energies in comparison with those calculated from the isolated molecule data. This enhancement may to some extent compensate the inaccuracies resulting from the use of minimal basis sets and will be discussed in the next section.

4. Discussion and Conclusions

For the discussion of the influence of the higher-order basis set superposition effects on the calculated interaction energies it is useful to consider the following ratios:

$$f_{ab}^{(1)} = \frac{E_{dd,a}^{(1)}}{E_{dd,b}^{(1)}}, \qquad f_{ac}^{(1)} = \frac{E_{dd,a}^{(1)}}{E_{dd,c}^{(1)}}, \tag{4}$$

and

$$f_{ab}^{(2)} = \frac{E_{did,a}^{(2)}}{E_{did,b}^{(2)}}, \qquad f_{ac}^{(2)} = \frac{E_{did,a}^{(2)}}{E_{did,c}^{(2)}}, \tag{5}$$

where $E_{dd,k}^{(1)}$ and $E_{did,k}^{(2)}$ $(k = a, b, c)$ are the classical dipole–dipole (dd) and dipole–induced–dipole (did) interaction energies [10], respectively. For each geometry of the water dimer they have been calculated with three different sets of the water molecule dipole moment and polarizability values. For $k = a$ the corresponding data follow from the dipole moments and polarizabilities computed in the water dimer minimal basis set (Tables 1 and 2). Hence, they account for the higher-order basis set superposition effects. For $k = b$ both the dipole moment and polarizability of H_2O are taken from the minimal basis set calculations on the isolated molecule (Table 1, $R_{OO} = \infty$). The case $k = c$ corresponds to the use of the near-HF dipole moment and polarizability of the isolated water

Table 3. Enhancement ratios for the dipole–dipole (*dd*) and dipole–induced–dipole (*did*) interaction energies in the water dimer calculated from different sets of the water molecule dipole moment and polarisability data[a]

	Configuration B				Configuration D			
R_{OO}(a.u.)	$f^{(1)}_{ab}$	$f^{(1)}_{ac}$	$f^{(2)}_{ab}$	$f^{(2)}_{ac}$	$f^{(1)}_{ab}$	$f^{(1)}_{ac}$	$f^{(2)}_{ab}$	$f^{(2)}_{ac}$
15.0	1.000	1.266	1.00	0.41	1.000	1.266	1.00	0.41
11.0	1.000	1.266	1.00	0.41	1.000	1.266	1.00	0.44
9.0	1.000	1.266	1.00	0.41	1.000	1.266	1.00	0.45
8.0	1.000	1.266	1.00	0.41	1.001	1.267	1.00	0.46
7.0	1.003	1.271	1.02	0.42	1.009	1.278	1.03	0.47
6.0	1.018	1.289	1.08	0.44	1.044	1.320	1.11	0.52
5.5	1.036	1.312	1.15	0.47	1.073	1.359	1.18	0.55
5.0	1.063	1.346	1.25	0.51	1.092	1.382	1.26	0.56
4.5	1.095	1.386	1.39	0.57	1.095	1.386	1.39	0.57

[a] For definitions of the enhancement ratios see Eqs. (4) and (5). The subscripts *a*, *b*, *c* at $f^{(1)}$ and $f^{(2)}$ correspond to different approximations used in the calculation of the *dd* and *did* interaction energies, respectively. See text for their explanation. Dimer geometries as shown in Fig. 1.

molecule [9] and gives the estimate of the accurate HF *dd* and *did* interaction energies.

The calculated enhancement ratios (4) and (5) are presented in Table 3. The (*ab*) ratios can be interpreted as a measure of the interaction energy enhancement arising from the higher-order superposition effects. The (*ac*) ratios illustrate the variation of the portion of accurate (*c*) interaction energies which is recovered in the approximation (*a*). It can be seen that for both configurations of the water dimer the higher-order basis set superposition effects are qualitatively the same. In both cases the enhancement of the *dd* and *did* interaction energies becomes important for regions close to the total SCF energy minima [1, 3] for the water dimer. Because of a similar behavior of the enhancement ratios for the two configurations the following discussion will be based on the data for configuration *B*. In this configuration Molecule 2 has a fixed angular position and all enhancement ratios are given by simple functions of R_{OO}.

According to the data of Table 3 the $f^{(2)}$ values increase much faster than the $f^{(1)}$ enhancement ratios. Since the minimal basis set calculations overestimate the *dd* energy and seriously underestimate the *did* interactions, it might be expected that for some values of R_{OO} what is gained in $E^{(1)}_{dd,a}$ will compensate the deficiency of $E^{(2)}_{did,a}$. However, the ratio $E^{(1)}_{dd,b}/E^{(2)}_{did,b}$ is approximately equal to 0.36 R^3_{OO} and shows that for the O · · · O distances of interest the overestimation of $E^{(1)}_{dd,a}$ will always play the dominant role. Slightly more favourable conditions occur when considering the corresponding ratio for accurate interaction energies. In this case one obtains $E^{(1)}_{dd,c}/E^{(2)}_{did,c} = 0.12\, R^3_{OO}$. Nonetheless, for the O · · · O distances close to the dimer SCF energy minimum, the *dd* interaction energy enhancement will be much larger than the deficiency of $E^{(2)}_{did,a}$. A complete compensation is rather unlikely to occur.

It has already been pointed out that the higher-order basis set superposition effects should not necessarily be regarded as the erratic contributions to the CP corrected minimal basis set results for SCF interaction energies. Indeed, they obviously improve the induction energies via the polarizability increase. However, the same effects also influence the dipole and higher multipole moments, and thus, they can overestimate the electrostatic contributions to the interaction energy. It follows that one can in fact profit from the higher-order basis set superposition effects provided the isolated molecule first-order properties are correctly represented in a given small basis set. Similar conclusions apply also to larger basis sets [3].

Finally, let us mention that the higher-order basis set superposition effects need to be carefully considered when investigating the interaction effects on different molecular properties, e.g. dipole moment or polarizability derivatives with respect to the vibration coordinates, nuclear magnetic shielding constants, etc. In that case the basis set superposition is certainly the unwanted effect on the calculated property changes that occur due to intermolecular interactions and the appropriate CP-type corrections must be applied.

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