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A new approach to the *ab initio* energy of the homodesmic reaction for the resonance energy of benzene

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Summary. A scheme of the basis set superposition error (BSSE) correction is first proposed and introduced to determine the *ab initio* energy of the homodesmic reaction for the resonance energy of benzene. Calculations with 6-31G*(5D) and 6-31G*(6D) basis sets at the complete fourth-order Møller–Plesset perturbation level furnish the energy value of 21.35 kcal/mol after the correction, which is in complete agreement with the experimental value of 21.3 ± 0.2 kcal/mol. The energy values at the lower theoretical levels are generally underestimated but they are superior to the uncorrected values. The inclusion of triple excitations displays the dominant contribution of the correlation energy. Detailed analysis of the results reveals some of the similarities between the homodesmic reaction of benzene and the interaction of van der Waals molecule, which provides further justification of the BSSE correction scheme presented in this study.

Key words: *Ab initio* – Benzene – Resonance energy – BSSE – Counterpoise correction

1. Introduction

The energy change ΔE in the following homodesmic reaction of benzene with ethylene to form butadiene is an approximation of the resonance energy of benzene [1]:

$$\text{benzene} + 3\ \text{ethylene} \rightarrow 3\ \text{butadiene}. \tag{1}$$

The experimental result of the enthalpy change ΔH in Eq. (1) is 21.2 ± 0.2 kcal/mol [1, 2]. Since the zero-point energy and thermal effects on the ΔH contribute only +0.2 kcal/mol the experimental energy change ΔE in Eq. (1) is estimated to be 21.3 ± 0.2 kcal/mol. However, *ab initio* calculations give a ΔE of 24.7 kcal/mol [3, 4] at the 6-31G* SCF and 28.9 kcal/mol [5] at the 6-31G* MP2 level (worse

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results by inclusion of the correlation energy). One would naturally speculate that this disagreement might be a consequence of the basis limitations and/or the truncation error of the Møller–Plesset expansions at the MP2 level. Disch and Schulman [6] have calculated the ΔE values at the same theoretical levels with various larger basis sets, 6-31G**, 6-31G**f, and 6-311G**. The results demonstrate that there is only a very small basis set dependence of the ΔE beyond the 6-31G* basis set (the successive ΔE values at the SCF level are 24.8, 24.5, 23.6 kcal/mol, and at MP2 28.7, 28.7, 28.0 kcal/mol). On the other hand, Haddon and Raghavachari [7] have studied the same problem in the basis set of 6-31G*(5D) through the MP4 level. Their successive ΔE values at the SCF, MP2, MP3, and MP4 levels are 24.8, 28.6, 23.4, and 24.3 kcal/mol, respectively. It does not show the converged value even at the MP4 level and furthermore the fourth-order value is poorer than the third-order value. Disch and Schulman [6] therefore concluded that the basis limitations are not the cause of the calculated ΔE problem and, instead, the truncation error of the Møller–Plesset expansions through the fourth-order is the dominant contribution to the problem. They suggested that higher levels of Møller–Plesset perturbation theory beyond the fourth-order are needed in order to achieve the ΔE value in agreement with experiment.

From the results of Haddon and Ragharachari, however, no immediate evidence can be seen from the higher order Møller–Plesset calculations beyond MP4 would positively bring down the overestimated ΔE value of 24.3 kcal/mol in MP4/6-31G*(5D) into the experimental range. This is because major corrections related to electron correlation effects would have been taken into account from SCF through MP4 calculations [8, 9] but, with the exception of the MP2 result, the calculated ΔE values stay almost the same at all levels of theory. The variances of the ΔE values are within 1.0 kcal/mol from SCF to MP3, and to MP4 while it actually needs −3.0 kcal/mol of correction to the MP4 result to achieve in agreement with experiment. There is no obvious reason why such a large correction term has to be introduced only after the fourth-order of Møller–Plesset expansions. According to convergence study by Handy et al. [10] and also by Laidig et al. [11], the sum of all the Møller–Plesset perturbation energy terms beyond the fourth-order is smaller than the fourth-order term. Therefore the MP4 result of ΔE is supposedly well converged and any improvement beyond it should be minor. As a conclusion, the disagreement of the calculated ΔE with experiment is still an interesting problem which is worth our further attention.

We are thinking about the above problem in a very different way. We consider that the basis set superposition error (BSSE) [12] in the above-mentioned calculations might have resulted in the serious disagreement with experiment. The BSSE problems are commonly known in calculations of the binding energies of weakly bound systems such as van der Waals molecules [13, 14]. However, the BSSE effects are always believed to be negligibly small and therefore not to be considered in calculations of regular chemical reactions. There are three main reasons that make us to consider that the BSSE is not negligible in calculations of this particular reaction, i.e., the homodesmic reaction of benzene. First, the reaction energy is relatively small as compared with other chemical reactions (21.3 kcal/mol vs. 60–100 kcal/mol). This means that the "overall" or net interaction involved with the reaction can be viewed as a weak interaction (for comparison, the energy of hydrogen bond is usually 5.0 kcal/mol) and that the relative magnitude of the BSSE versus the interaction energy itself is larger than that in other regular chemical reactions. The second reason is that the benzene molecule is potentially subject to the large BSSE effect due to its unique structural arrangement. As it is known, the BSSE results from the extension of basis of one part of a molecule to the orbital space of the other part (each is considered as an integral part in question of the interaction or reaction). Benzene is a highly symmetrical and compact molecule while its "dissociation product", butadiene, is a loose linear molecule. Therefore we expect that a relatively large unphysical energy lowering, as a BSSE, would be "contaminated" in the calculated total energy of benzene due to the mutual extensions of basis to the orbital space of different parts of the molecule. Finally, it should be noted that the calculated ΔE values achieved so far are all systematically overestimated. This means that there is a possible hidden factor which has caused the systematic calculational errors. The BSSE effect is known to be such a factor causing systematic overestimations of the calculated binding energies as demonstrated in van der Waals molecular studies [13, 14].

To find out the numerical value of the BSSE in benzene and to make correction may not be as easy as it is usually in van der Waals molecular studies. The benzene molecule does not have any direct structural relations to its partner molecules, i.e., butadiene and ethylene, and so the counterpoise technique cannot be applied directly to determine the BSSE. In fact, by far no explicit method has been proposed to treat the BSSE problems in such a complicated chemical reaction. In this work, we will develop a possible method to find the value of the BSSE correction for the ΔE of reaction (1) in the light of Boys and Bernardi's full function counterpoise (CP) procedure [15]. This method can be easily generalized to study the BSSE problems in other complicated chemical reactions.

2. Method

The ΔE of Eq. (1) is given as:

$$\Delta E = 3E_4 - (E_6 - 3E_2), \tag{2}$$

where E_4, E_6, and E_2 are the total energies of butadiene, benzene, and ethylene, respectively. In order to remove the BSSE in Eq. (2), a correction δ must be made to ΔE, i.e.:

$$\Delta E(\text{corrected}) = \Delta E + \delta. \tag{3}$$

Depending on the choice of reference energy and the interpretation of BSSE, there are several approaches to get the correction δ. Determination of the absolute BSSE value for each molecule is not practical nor necessary. Therefore our primary strategy is to correct for the inconsistency of BSSE among the molecules involved in the reaction, namely in our case, benzene, butadiene, and ethylene, by determining the relative BSSE values of the individual molecules. Since both of our main nuclear frameworks of benzene and butadiene consist of the ethylene-like basic repeat unit, we choose the energy of ethylene as the reference. In other words, we assume that the BSSE value of ethylene is zero and therefore no BSSE correction should be made to the ethylene energy. The BSSE corrections should be made only to the energies of benzene and butadiene. In order to determine the individual BSSE corrections for the energies of benzene and butadiene, several structures are defined in Fig. 1 for counterpoise calculations. Structures ***A***, ***B***, ***B′*** are the same C_2H_2 unit, a fragment of benzene, in

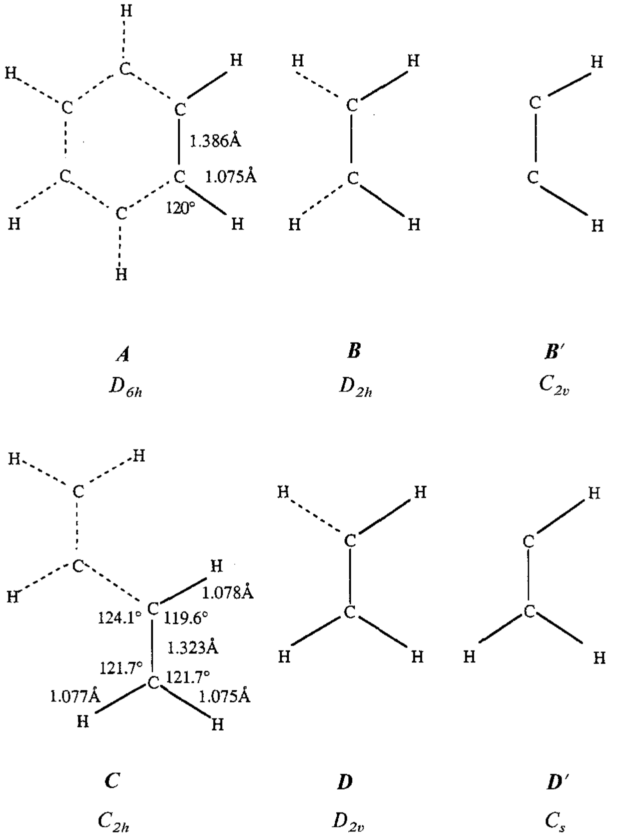

Fig. 1. Structures for counterpoise calculations. Atoms by *dotted lines* are ghost atoms. Symmetries of the structures are indicated with the ghost atoms

three different basis environments. They are designed to determine the BSSE value of benzene. Structure *A* attaches a set of the C_4H_4 ghost atoms which are so positioned that the whole geometry of *A* is a replica of benzene. Note that all the ghost atoms in Fig. 1 are connected by the dotted lines instead of the solid lines. Structure ***B*** is formed from *A* by replacing the entire C_4H_4 ghost atoms in *A* with two hydrogen ghost atoms, which are so positioned that the overall symmetry of ***B*** is D_{2h} as it is for ethylene. Structure ***B′*** is formed from ***B*** by just removing the two hydrogen ghost atoms in ***B***, or from *A* by removing the whole ghost atoms in *A*. Structures ***C***, ***D***, ***D′*** are the same C_2H_3 unit, a half of butadiene, in three other different basis environments. They are designed to determine the BSSE value of butadiene. Structure ***C*** attaches the other half of butadiene as a set of ghost atoms, which are so positioned that the whole geometry of ***C*** is a replica of butadiene. Structure ***D*** is formed from ***C*** by replacing the entire C_2H_3 ghost atoms in ***C*** with a single hydrogen ghost atom, which is positioned at the point symmetrical to the other hydrogen in regard with the C–C axis. Structure ***D′*** is formed from ***D*** by removing the hydrogen ghost atom in ***D***, or from ***C*** by removing the whole ghost atoms in ***C***.

In order to make the BSSE correction to the benzene energy, we first define a quantity δ_a as the energy difference of the structures *A* and ***B*** in Fig. 1:

$$\delta_a = E_A - E_B, \tag{4}$$

We can view the δ_a as the extra energy lowering of one C_2H_2 unit in the environment of benzene due to the basis extension from the other two C_2H_2 units, as compared to that of the same C_2H_2 unit in the environment of ethylene due to the basis extension from the other two hydrogen atoms. Since there are three pairs of such mutual basis extensions in the calculation of the whole benzene energy, the total BSSE correction to the benzene energy should be:

$$\delta_6 = 3\delta_a, \tag{5}$$

and then the corrected benzene energy is:

$$E_6(\text{corrected}) = E_6 - 3\delta_a. \tag{6}$$

Quite similarly, in order to make the BSSE correction to the butadiene energy, we define another quantity δ_b to be the energy difference of structure ***C*** and ***D*** in Fig. 1:

$$\delta_b = E_{\boldsymbol{C}} - E_{\boldsymbol{D}}. \tag{7}$$

Again we can view the δ_b as the extra energy lowering of one C_2H_3 unit in the environment of butadiene due to the basis extension from the other C_2H_3 unit, as compared to that of the same C_2H_3 unit in ethylene due to the basis extension from the other hydrogen atom. Since there are two pairs of such mutual basis extensions in the calculation of the whole butadiene energy, the total BSSE correction to the butadiene energy should be:

$$\delta_4 = 2\delta_b, \tag{8}$$

and then the corrected butadiene energy:

$$E_4(\text{corrected}) = E_4 - 2\delta_b. \tag{9}$$

With Eqs. (6) and (9), the corrected energy change in Eq. (1) is then given by:

$$\Delta E(\text{corrected}) = \Delta E + (3\delta_a - 6\delta_b), \tag{10}$$

where the ΔE on the right hand side is given by Eq. (2). Compared with Eq. (3), the overall BSSE correction for the ΔE in Eq. (1) is:

$$\delta = 3\delta_a - 6\delta_b. \tag{11}$$

We also designed an alternative approach to the determination of the relative BSSE values of benzene and butadiene. In the alternative approach, structures ***B′*** and ***D′*** are used to replace the reference structures ***B*** and ***D***. The formulation of this approach follows exactly the same procedure as described above for the first approach. The corresponding notations for the variables used by the alternative approach are designated by a prime (′) in order to identify them from those in the first approach. It should be pointed out that the alternative approach is less favorable for the fact that the bases of the reference structures ***B′*** and ***D′*** are not balanced to give a consistent account of the BSSE correction in benzene and in butadiene. Namely, the reference used for the BSSE of benzene is C_2H_2 while that for the BSSE of butadiene is C_2H_3. Under this condition, the BSSE of ethylene should be non-zero but it cannot be determined because of the ambiguity of two references. There are two reasons that make us consider this alternative approach. First, structure ***B′*** and ***D′*** are the direct fragments of their parent structures of benzene and butadiene, respectively. This provides us the direct relationship of structures and quantities involved and so the clear picture of the whole strategy used in this study. The second reason is that we want to use the alternative approach as a control test for the reliability of the method proposed in this study. A less favorable approach is supposed to produce less favorable results if the whole strategy of the method is correct. The results could not be dramatically off because the unfavorable factor, a difference of the hydrogen basis between ***B'*** and ***D'***, is not very large. Nevertheless, our concentration of this study and emphasis of analysis for the results will be mainly focused on the first approach of BSSE correction.

It should be pointed out that even in the first approach of BSSE correction there is still a slight imbalance of the reference. The geometrical parameters of reference structure ***B*** for the BSSE of benzene, e.g., the C–C bond length and the HCH bond angles, are different to that of reference structure ***D*** for the BSSE of butadiene, and the geometrical parameters of both reference structures are further different to that of ethylene. For example, the C–C bond length is 1.386 Å in ***B***, 1.323 Å in ***D***, and 1.317 Å in ethylene. Therefore the corrected benzene energy by Eq. (6) and the corrected butadiene energy by Eq. (9) as well as the ethylene energy are subject to higher-order correction for BSSE. We will not consider the higher-order correction for BSSE in this work since these structural changes are small. It is likely that the contributions of higher-order correction for BSSE to the energy change of Eq. (1) are mostly cancelled out. For example, 3 pairs of "long" C–C in benzene plus 3 pairs of "short" C–C in 3 ethylenes are balanced by 6 pairs of "medium" C–C.

The HF/6-31G* optimized molecular geometries of benzene, butadiene and ethylene [3] are used throughout in this work. The corresponding geometrical parameters of benzene and butadiene were also used in defining structures ***A***, ***B***, ***B'***, ***C***, ***D***, and ***D'*** (for details, see Fig. 1). Two standard basis sets, 6-31G*(5D) and 6-31G*(6D) [16, 17], were employed. The difference between the two basis sets is that a set of five *d*-type functions, z^2, x^2, y^2, *xy*, *yz*, and *zx*, is used in 6-31G*(5D) while a set of six *d*-type functions, x^2, y^2, z^2, *xy*, *yz*, and *zx*, is used in 6-31G*(6D). The net difference is that 6-31G*(6D) has an additional *s*-type Gaussian function as compared to 6-31G*(5D). Electron correlation effects were included by Møller–Plesset (MP) perturbation theory up to the complete fourth-order level [8, 9]. All calculated energies are given at the Hartree–Fock (HF) level and the correlated levels of the second-order Møller–Plesset perturbation (MP2), the third-order (MP3), the fourth-order with double and quadruple excitations (MP4DQ), the fourth-order with single, double, and quadruple excitations (MP4SDQ), and the fourth-order with single, double, triple, and quadruple excitations (MP4SDTQ, or the complete MP4).

3. Results and discussion

Table 1 contains the total energies of benzene, butadiene, and ethylene in the two basis sets, 6-31G*(5D) and 6-31G*(6D), at the HF, MP2, MP3, MP4DQ, MP4SDQ, and MP4SDTQ levels. As it is seen in the Table, all the energies are monotonically improved (lowered) with the increase of theoretical level for electron correlation. The energy improvements from 6-31G*(5D) to 6-31G*(6D) are greater at the correlated levels than at the Hartree–Fock level. For example, the improvement of the benzene energy from MP2/6-31G*(5D) to MP2/6-31G*(6D) is 0.00876 Hartree (5.50 kcal/mol), which is much larger than 0.00056 Hartree (0.35 kcal/mol) correspondingly at the HF level. This indicates certain diversity of the two basis sets used for the study in this work.

Table 1. Total energies of benzene, butadiene, and ethylene (in Hartrees)

Basis/level	Benzene	Butadiene	Ethylene
6-31G*(5D)			
HF	−230.70249	−154.91904	−78.03136
MP2	−231.44764	−155.41536	−78.28151
MP3	−231.47815	−155.44996	−78.30311
MP4DQ	−231.47763	−155.45293	−78.30567
MP4SDQ	−231.48455	−155.45792	−78.30814
MP4SDTQ	−231.52082	−155.47643	−78.31589
6-31G*(5D)			
HF	−230.70314	−154.91965	−78.03172
MP2	−231.45642	−155.42118	−78.28435
MP3	−231.48515	−155.45458	−78.30536
MP4DQ	−231.49456	−155.45750	−78.30799
MP4SDQ	−231.49198	−155.46287	−78.31055
MP4SDTQ	−231.52988	−155.48221	−78.31870

Table 2 contains the energies of all counterpoise structures (shown in Fig. 1) in the two basis sets at the HF, MP2, MP3, MP4DQ, MP4SDQ, and MP4SDTQ levels. As it is expected, the energy of ***A*** is lowered from that of ***B*** due to the larger ghost atom basis used by ***A*** in the counterpoise calculations. The energy of ***B′*** is the highest as compared to that of ***A*** and ***B*** since no ghost atom basis is used by ***B′***. For the same reason, the energy of ***C*** is lowered from that of ***D***, and the energy of ***D′*** is the highest among that of ***C***, ***D***, and ***D′***. The relative energy differences between these counterpoise structures, which are defined as δ_a and δ_b in Eqs. (4) and (7) respectively, are summarized in Table 3. As it is seen in this table, the δ_a and δ_b values are always larger at the correlated levels than they are at the HF level. This is in agreement with the general result in

Table 2. Energies of the counterpoise structures (in Hartrees)

Basis/level	Counterpoise structures					
	A	***B***	***B′***	***C***	***D***	***D′***
6-31G*(5D)						
HF	−76.66814	−76.66418	−76.66322	−77.38613	−77.38557	−77.38531
MP2	−76.97712	−76.96906	−76.96574	−77.59897	−77.59593	−77.59467
MP3	−76.96875	−76.96018	−76.95704	−77.62170	−77.61849	−77.61716
MP4DQ	−76.97524	−76.96752	−76.96463	−77.62445	−77.62132	−77.62000
MP4SDQ	−76.98334	−76.97568	−76.97284	−77.62808	−77.62488	−77.62353
MP4SDTQ	−77.00706	−76.99850	−76.99517	−77.63425	−77.63084	−77.62939
6-31G*(6D)						
HF	−76.66830	−76.66429	−76.66337	−77.38643	−77.38586	−77.38561
MP2	−76.98003	−76.97170	−76.96831	−77.60175	−77.59860	−77.59733
MP3	−76.97080	−76.96199	−76.95883	−77.62399	−77.62069	−77.61935
MP4DQ	−76.97740	−76.96946	−76.96653	−77.62669	−77.62347	−77.62215
MP4SDQ	−76.98575	−76.97788	−76.97499	−77.63505	−77.62721	−77.62585
MP4SDTQ	−77.01016	−77.00135	−76.99798	−77.63698	−77.63347	−77.63201

Table 3. Function counterpoise corrections δ_a and δ_b (in kcal/mol)

Basis/level	δ_a	δ_b	δ'_a	δ'_b
6-31G*(5D)				
HF	−2.49	−0.35	−3.09	−0.52
MP2	−5.06	−1.91	−7.14	−2.70
MP3	−5.38	−2.01	−7.35	−2.85
MP4DQ	−4.84	−1.96	−6.66	−2.79
MP4SDQ	−4.80	−2.01	−6.59	−2.85
MP4SDTQ	−5.37	−2.14	−7.46	−3.05
6-31G*(6D)				
HF	−2.51	−0.36	−3.10	−0.51
MP2	−5.23	−1.97	−7.35	−2.77
MP3	−5.53	−2.07	−7.52	−2.91
MP4DQ	−4.98	−2.02	−6.82	−2.85
MP4SDQ	−4.94	−2.07	−6.75	−2.92
MP4SDTQ	−5.53	−2.21	−7.64	−3.12

calculations of van der Waals molecular interactions. It is very interesting to see that the δ_a values are much larger than (more than double) the corresponding δ_b values. The δ_a would be expected to be double δ_b because the differential of ghost atom basis between $\boldsymbol{A}$ and $\boldsymbol{B}$ is double that between $\boldsymbol{C}$ and $\boldsymbol{D}$ (refer to Eq. (11)). The extra amount of δ_a gained from our calculations may be contributed from the distinct structural arrangement in the benzene molecule, i.e. the structure of high symmetry and compactness, which favors the energy lowering by the BSSE effect. This is just in agreement with our earlier expectation.

Following the procedure described in Sect. 2 with the results in Table 1, Table 2, and Table 3, the energy of Eq. (1) before BSSE correction, ΔE, and after BSSE correction, ΔE(corrected), are calculated and summarized in Table 4. The overall BSSE correction δ, defined by Eqs. (3) and (11), is also given in

Table 4. Calculated energies of Eq. (1) before and after BSSE corrections (in kcal/mol)

Basis/level	ΔE	δ	ΔE(corrected)	δ'	$\Delta E'$(corrected)
6-31G*(5D)					
HF	24.76	−5.37	19.39	−6.18	18.58
MP2	28.91	−3.71	25.20	−5.22	23.69
MP3	23.60	−4.06	19.54	−4.95	18.65
MP4DQ	22.67	−2.75	19.92	−3.23	19.44
MP4SDQ	22.08	−2.35	19.74	−2.61	19.47
MP4SDTQ	24.60	−3.25	21.35	−4.09	20.51
6-31G*(6D)					
HF	24.68	−5.42	19.26	−6.22	18.46
MP2	28.81	−3.85	24.96	−5.42	23.39
MP3	23.52	−4.17	19.35	−5.09	18.42
MP4DQ	22.61	−2.84	19.77	−3.39	19.22
MP4SDQ	21.98	−2.43	19.55	−2.74	19.24
MP4SDTQ	24.70	−3.35	21.35	−4.23	20.47

Table 4 with the corresponding ΔE(corrected). As it is seen in the table, the ΔE values before BSSE correction are consistent with the results by other authors and are all overestimated. There is a very small difference of the ΔE or ΔE(corrected) results between the two basis sets, which indicates the very small basis set dependence of the ΔE and ΔE(corrected) at the HF level and up to MP4SDTQ level. This is in agreement with the conclusion by Disch and Schulman [6]. The ΔE results at MP4DQ and MP4SDQ which are absent in the report by Haddon and Raghavachari, 22.67 and 22.08 kcal/mol in 6-31G*(5D) or 22.76 and 21.98 kcal/mol in 6-31G*(6D), respectively, unexpectedly show slightly better agreement with experiment than the results of all other theoretical levels. But, like other ΔE results, they are overestimated too. Substantial overall BSSE corrections, $\delta = -2.35$ to -5.42 kcal/mol, are obtained to correct for ΔE. The overestimated ΔE values are therefore brought down to give the corresponding values of ΔE(corrected), which are generally underestimated but overall in better agreement with experiment with the exception of MP2 results. The ΔE(corrected) values at MP2 in the two basis sets are improved by about 3.8 kcal/mol through BSSE corrections but are still overestimated since the overestimations by ΔE are too large. Therefore there are likely other major sources of error in addition to the BSSE effect that exist in the calculations at the MP2 level. The ΔE(corrected) values at HF, MP3, MP4DQ, and MP4SDQ, being underestimated by 1.5–2.2 kcal/mol (or 7–10%) show certain superiority to the corresponding uncorrected ΔE values. Among them, the HF results, 19.39 kcal/mol in 6-31G*(5D) and 19.26 kcal/mol in 6-31G*(6D), are the lowest and least favorable with the underestimations of 2.1–2.2 kcal/mol. But they are preferred to the uncorrelated HF results since the undercorrelations by ΔE(corrected) is smaller in magnitude than the overcorrections by ΔE (3.2–3.3 kcal/mol). The ΔE(corrected) values at MP4DQ and MP4SDQ show a continuing improvement over the MP3 results. Note that the values of the overall BSSE correction δ are the smallest at the MP4DQ and MP4SDQ levels. The most striking results are achieved at MP4SDTQ, the highest theoretical level of electron correlation used in this study. The MP4SDTQ calculations in both of the basis sets have furnished the same ΔE(corrected) value of 21.35 kcal/mol, which is in complete agreement with experiment. It is very interesting to note that the major improvement of ΔE(corrected) is not achieved until the triply excited configurations (or triple excitations) for electron correlation are included in the complete fourth-order Møller–Plesset perturbation.

One would wonder why the ΔE(corrected) values after BSSE corrections are mostly underestimated at the lower levels of theory and why they show a slight but gradual improvement with the increase of theoretical level for electron correlation, which is quite in contrast to the uncorrelated ΔE values. One would also wonder why the inclusion of triple excitations in electron correlation is so decisive in the accurate determination of the ΔE(corrected). The following analysis based on the experience in calculations of van der Waals interactions may provide some of the clues to above questions and therefore lead to a comprehensive understanding of the calculational results. It may also be helpful to the justification of the entire scheme of BSSE correction presented in this work.

It is known that Boys and Bernardi's full counterpoise (CP) procedure for BSSE correction usually produces underestimated binding energies of van der Waals molecules. Such underestimations may be contributed from three possible sources of error: the limitation of basis set, the deficiency of the theory for electron correlation, and the overestimation of the true BSSE by the CP method. As noted in our introduction, the work by Disch and Schulman [6] has demonstrated that the 6-31G* basis set used by this work is already saturated for the calculation of the reaction energy ΔE. Therefore the limitation of basis set may be excluded from the problem of this work. In fact, for large molecular systems such as benzene and butadiene, the basis requirements are less extreme than for small systems because of the high flexibility of the basis functions in the polyatomic systems. The issue of whether the CP method overcorrects for the true BSSE has long been a very controversial topic among theoretical researchers in the area. We demonstrated [18] that the overcorrection for the BSSE by the CP method is negligibly small as compared to the error from the use of insufficient basis set and it is therefore totally negligible when a sufficiently large basis set is employed. As a result, it is the limitation of the theory for electon correlation that has caused the underestimations of the ΔE(correlated) at the HF, MP3, MP4DQ, and MP4SDQ levels. Let us look at the performance of the Møller–Plesset perturbation theory on the study of the neon dimer at the equilibrium distance [19]. The MP2 calculation only recovers 65% of the binding energy, MP3 recovers 80%, MP4DQ or MP4SDQ recovers 85%, and MP4SDTQ recovers over 98%. The similar performance is also displayed by the ΔE(corrected) results in this work. For example, the ΔE(corrected) values in 6-31G*(5D) are 19.39, 19.54, 19.92 (or 19.74), and 21.35 kcal/mol at HF, MP3, MP4DQ (or MP4SDQ), and MP4SDTQ levels, respectively. Such a gradual improvement of the ΔE(corrected) with the increase of theoretical level demonstrates a strong similarity between the determination of the energy of Eq. (1) and that of the interaction energy of a van der Waals molecule. The difference is that the energy of Eq. (1) is characterized by the dominant contribution from the HF energy, ~19.3 kcal/mol, and the less important contribution from the correlation energy, ~2.0 kcal/mol.

In the calculation of van der Waals molecular interaction energy, the coupling between the inter- and intramolecular electron correlations is one of the major contributions to the calculated interaction energy [20, 21]. This coupling can be introduced at the MP4 level by inclusion of the triple excitations in the theory of electron correlation. Neglecting triple excitations results in unrealistic values of interaction energy in the region of van der Waals minimum and at shorter distances. It is seen from our results of ΔE(corrected) that the inclusion of triple excitations has indeed played a dominant role in providing an accurate account of the correlation energy contribution to ΔE(corrected). In fact, the major part of the correlation energy contribution in ΔE(corrected), ~1.6 kcal/mol out of ~2.0 kcal/mol, is from the inclusion of triple excitations at the MP4SDTQ level. The single, double, and quadruple excitations altogether have contributed less than 0.5 kcal/mol. The relative importance of the triples vs. other excitations is larger in our ΔE(corrected) than in van der Waals interaction energy. This can be understood by the fact that the role of triple excitations is increasingly important as the distance decreases in a van der Waals molecule [22]. It is obvious that the distance between the C_2H_2 units in benzene is much shorter than the distance considered in a van der Waals molecule. Another fact about the role of triple excitations in the van der Waals molecular study is that it is sensitive to the basis set used in the calculation [23]. This means that the role of triple excitations could be enhanced by use of a good basis set or suppressed by use of a bad basis set. It is seen in our results that the improvements of ΔE(corrected) from MP4SDQ to MP4SDTQ are 1.61 kcal/mol in 6-31G*(5D) and 1.80 kcal/mol in 6-31G*(6D), respectively. Meantime, the improvements of ΔE(corrected) with other increases of theoretical level, say, from MP3 to MP4SDQ, are nearly the same with the two basis sets. This clearly demonstrates the basis sensitivity of the role of triple excitations in ΔE(corrected), which is parallel to that in the van der Waals molecular study. By the way, it should be pointed out that the performance of correlation calculations with 6-31G*(5D) is not truly superior to that with 6-31G*(6D) as it appears in the ΔE(corrected). It is the slightly higher HF value in 6-31G*(5D) (19.39 kcal/mol, compared to 19.26 kcal/mol in 6-31G*(6D)) that makes all the 6-31G*(5D) values at the correlated levels look slightly and consistently better than the corresponding 6-31G*(6D) values.

We now finally take a look into the results from the alternative approach of BSSE correction. As mentioned before, this approach is less favorable for the BSSE correction in our problem because of the imbalance of references considered. Just as we have expected, the $\Delta E'$(corrected) values given in Table 4 are indeed generally inferior to the ΔE(corrected) values corresponding to the respective theoretical levels. It is likely that the alternative BSSE correction has overestimated the true BSSE inconsistency in the ΔE for Eq. (1). However, the overestimations, ranging from 0.3 to 0.9 kcal/mol with the exclusion of MP2 results, are not too serious and the $\Delta E'$(corrected) values still show some supriority to the uncorrelated ΔE values, respectively. One of the interesting points is the smooth, gradual and monotonic improvement of $\Delta E'$(corrected) with the increase of theoretical level for electron correlation. In reality, to find a balanced reference structure for BSSE correlations is a hard task for the majority of regular chemical reactions and it is even impossible in some cases. The results from this alternative approach of BSSE correction tell us that a less favorable BSSE correction scheme based on the use of not fully balanced reference structure is still feasible to produce results superior to the uncorrelated results.

4. Conclusions

We have presented in this study a novel approach to the problem of *ab initio* energy of the homodesmic reaction of benzene for the resonance energy of benzene. The primary point of view initiating this study is that the BSSE has caused the systematic overestimation of the energy in the conventional *ab initio* calculations. The main reason in support of this point of view is that the high symmetry and compactness of the benzene molecule in comparison with the butadiene molecule could result in the relatively larger BSSE effect in the evaluation of its energy that could not be balanced by the BSSE in butadiene. A scheme of BSSE correction is therefore proposed in the spirit of Boys and Bernardi's counterpoise method and applied to the determination of the *ab initio* energy of the homodesmic reaction of benzene. The fundamental procedure in the BSSE correction scheme is the choice of reference and the determination of the structures for counterpoise calculations in order to determine the relative BSSE values of the individual molecules.

The calculational results after the BSSE correction are in complete agreement with experiment at the MP4SDTQ level. The results at the HF level and up to the MP4SDQ level are generally underestimated due to the deficiency of electron correlation. The contribution of correlation energy to the reaction energy is dominated by the inclusion of triple excitations. They could be understood by comparisons with the calculation of the van der Waals interactions. Further detailed analysis of the results reveals several similarities in the calculations between the homodesmic reaction of benzene and the interactions of van der Waals molecules, which may serve as the additional justification of the BSSE correction scheme proposed in this study.

The approach of the present study may not be limited to the specific problem as in the homodesmic reaction of benzene. In our point of view, virtually all chemical processes studied by *ab initio* calculations are involved with the BSSE effects. In fact, comparisons between the calculated and experimental bond separation energies for other systems [24] all show the similar preference of the calculated energy for the larger and more compact species involved in a reaction. Now that the BSSE effects are prevalently concerned in calculations of van der Waals interactions there should be no exception for the regular chemical reactions. However, it is different for most chemical reactions in that the contributions of the BSSE effects are small and balanced from the reactant(s) to the product(s) and therefore the overall contributions to the reaction energies are negligible. In order to prove it, we have applied the BSSE correction scheme to the study of two other reactions. The first is the reaction of hydrogen with fluorine to form hydrogen fluoride: $H_2 + F_2 = 2\,HF$. The overall BSSE correction (equivalent to δ in the case of the benzene reaction) contributes only 0.1 kcal/mol to the reaction energy (about 133 kcal/mol) despite the observation that individual correction terms (equivalent to $3\delta_a$ or $6\delta_b$) are as large as 10 kcal/mol. The second is the reaction of ethylene with methane to form ethane $CH_2{=}CH_2 + 2\,CH_4 = 2\,CH_3CH_3$. The overall BSSE correction contributes about 0.5 kcal/mol to the reaction energy (about 20 kcal/mol).

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