Theor Chem Acc (2001) 106: 301–313
DOI 10.1007/s002140100280

Theoretical
Chemistry Accounts

*Regular article*

# The effect of basis set superposition error on the convergence of interaction energies

**Masao Masamura**

Department of Preventive Dentistry, Okayama University Dental School, Shikata-cho 2-5-1, Okayama 700-8525, Japan
e-mail: ep7@dent.okayama-u.ac.jp

Received: 14 March 2001 / Accepted: 25 April 2001 /

**Abstract.** For the intermolecular interaction energies of ion-water clusters [$OH^{-}(H_2O)_n$ (n = 1,2), $F^{-}(H_2O)$, $Cl^{-}(H_2O)$, $H_3O^{+}(H_2O)_n$ ($n = 1,2$), and $NH_4{}^{+}(H_2O)_n$ ($n = 1,2$)] calculated with correlation-consistent basis sets at MP2, MP4, QCISD(T), and CCSD(T) levels, the basis set superposition error is nearly zero in the complete basis set (CBS) limit. That is, the counterpoise-uncorrected intermolecular interaction energies are nearly equal to the counterpoise-corrected intermolecular interaction energies in the CBS limit. When the basis set is smaller, the counterpoise-uncorrected intermolecular interaction energies are more reliable than the counterpoise-corrected intermolecular interaction energies. The counterpoise-uncorrected intermolecular interaction energies evaluated using the MP2/aug-cc-pVDZ level is reliable.

**Key words:** Basis set superposition error – Counterpoise – Intermolecular interaction energies – Ion-water clusters – Correlation-consistent basis sets

## 1 Introduction

The intermolecular interaction energy of ion-water clusters is important for understanding biological phenomena. One problem in the computation of intermolecular interaction energy is the uncertainly caused by basis set superposition error (BSSE) [1]. The BSSE correction can be estimated using the counterpoise method [2]. Although this approach is still regarded with some skepticism, there is nowadays common agreement that the counterpoise method is a useful procedure for correcting for BSSE [3]. In the limit of a complete basis, the BSSE would be zero and it is expected that the counterpoise-uncorrected intermolecular interaction energies are equal to the counterpoise-corrected intermolecular interaction energies [4].

For enthalpy changes of $CH_3O^{-}(H_2O)_n$ ($n = 1,2$) evaluated using MP2/aug-cc-pVDZ level and $CH_3S^{-}(H_2O)_n$ ($n = 1,2,3$) evaluated using the MP2/6-31++G(2d,2p) level, the counterpoise-corrected values are worse than the uncorrected values [5].

For $OH^{-}(H_2O)_n$ ($n = 1,2$), the counterpoise-uncorrected intermolecular interaction energies evaluated using the MP2/aug-cc-pVDZ level are reliable because the counterpoise-uncorrected intermolecular interaction energies evaluated at the MP2/aug-cc-pVDZ level are close to the counterpoise-corrected intermolecular interaction energies evaluated using the MP2/aug-cc-pV5Z level [6].

The objectives of this article are threefold. First, we show that for the intermolecular interaction energies of ion-water clusters [$OH^{-}(H_2O)_n$ ($n = 1,2$), $F^{-}(H_2O)$, $Cl^{-}(H_2O)$, $H_3O^{+}(H_2O)_n$ ($n = 1,2$), and $NH_4{}^{+}(H_2O)_n$ ($n = 1,2$)] calculated with correlation-consistent basis sets [7–11] at the MP2 [12–16], MP4 [17], QCISD(T) [18], and CCSD(T) [19] levels, the BSSE is nearly zero in the complete basis set (CBS) limit. That is, the counterpoise-uncorrected intermolecular interaction energies are nearly equal to the counterpoise-corrected intermolecular interaction energies in the CBS limit. Second, we show that when the basis set is smaller, the counterpoise-uncorrected intermolecular interaction energies are more reliable than the counterpoise-corrected intermolecular interaction energies. Third, we show that the counterpoise-uncorrected intermolecular interaction energies evaluated using the MP2/aug-cc-pVDZ level are reliable.

These results are important because it is expected that they hold for other ion-water clusters.

## 2 Methods

We used the Gaussian 94 [20], Gaussian 98 [21], and Molpro 96 [22] programs, on the SX-5, VPP5000, SGI2800, and HPC computers at the Research Center for Computational Science. We carried out full geometry optimizations using MP2/aug-cc-pVDZ and MP2/6-311++G(d,p) [23] levels for $OH^{-}(H_2O)_n$ ($n = 0$–$2$), $H_3O^{+}(H_2O)_n$ ($n = 0$–$2$), $NH_4{}^{+}(H_2O)_n$ ($n = 0$–$2$), and $H_2O$ in Fig. 1. The core electrons were frozen. We also performed vibrational analysis for all species at the optimized structures to confirm that all vibrational frequencies are real.

Next, we performed MP2/aug-cc-pV*x*Z, MP4SDTQ/aug-cc-pV*x*Z, QCISD(T)/aug-cc-pV*x*Z, CCSD(T)/aug-cc-pV*x*Z, and

B3LYP/aug-cc-pV$x$Z [24] ($x$ = D,T,Q,5,6) energy calculations at the MP2/aug-cc-pVDZ geometries. Similar calculations were performed using the 6-311++G(d,p), 6-311++G(2d,2p), 6-311++G(3d,3p), and 6-311++G(3df,3pd) basis sets [23] at the MP2/6-311++G(d,p) geometries.

The intermolecular interaction energy ($\Delta E_{n-1,n}$) of $OH^-(H_2O)_n$ was calculated by the following formula:

$$\Delta E_{n-1,n} = E[OH^-(H_2O)_n] - E[OH^-(H_2O)_{n-1}] - E(H_2O) \ .$$

The CBS limit was estimated on the basis of Ref. [25]. BSSE was corrected using the counterpoise method [2, 26]. Similar calculations were performed for $H_3O^+(H_2O)_n$ and $NH_4^+(H_2O)_n$.

## 3 Results

All the species considered here have all real vibrational frequencies and correspond to equilibrium structures.

### *3.1 $OH^-(H_2O)_n$*

The counterpoise-uncorrected and counterpoise-corrected intermolecular interaction energies and the BSSE for $OH^-(H_2O)_n$ ($n = 1,2$) evaluated using the aug-cc-pV$x$Z ($x$ = D,T,Q,5,6), 6-311++G(d,p), 6-311++G(2d,2p), 6-311++G(3d,3p), and 6-311++G(3df,3pd) basis sets at the MP2, MP4, QCISD(T), CCSD(T), and B3LYP levels are shown in Tables 1 and 2.

For the intermolecular interaction energy of $OH^-(H_2O)$ calculated using the aug-cc-pV$x$Z ($x$ = D,T,Q,5,6) basis sets at the MP2, MP4, QCISD(T), and CCSD(T) levels, the BSSE is nearly zero in the CBS limit (Fig. 2). In addition, the counterpoise-uncorrected intermolecular interaction energies are nearly equal to the counterpoise-corrected intermolecular interaction energies in the CBS limit (Fig. 2). When the basis set is

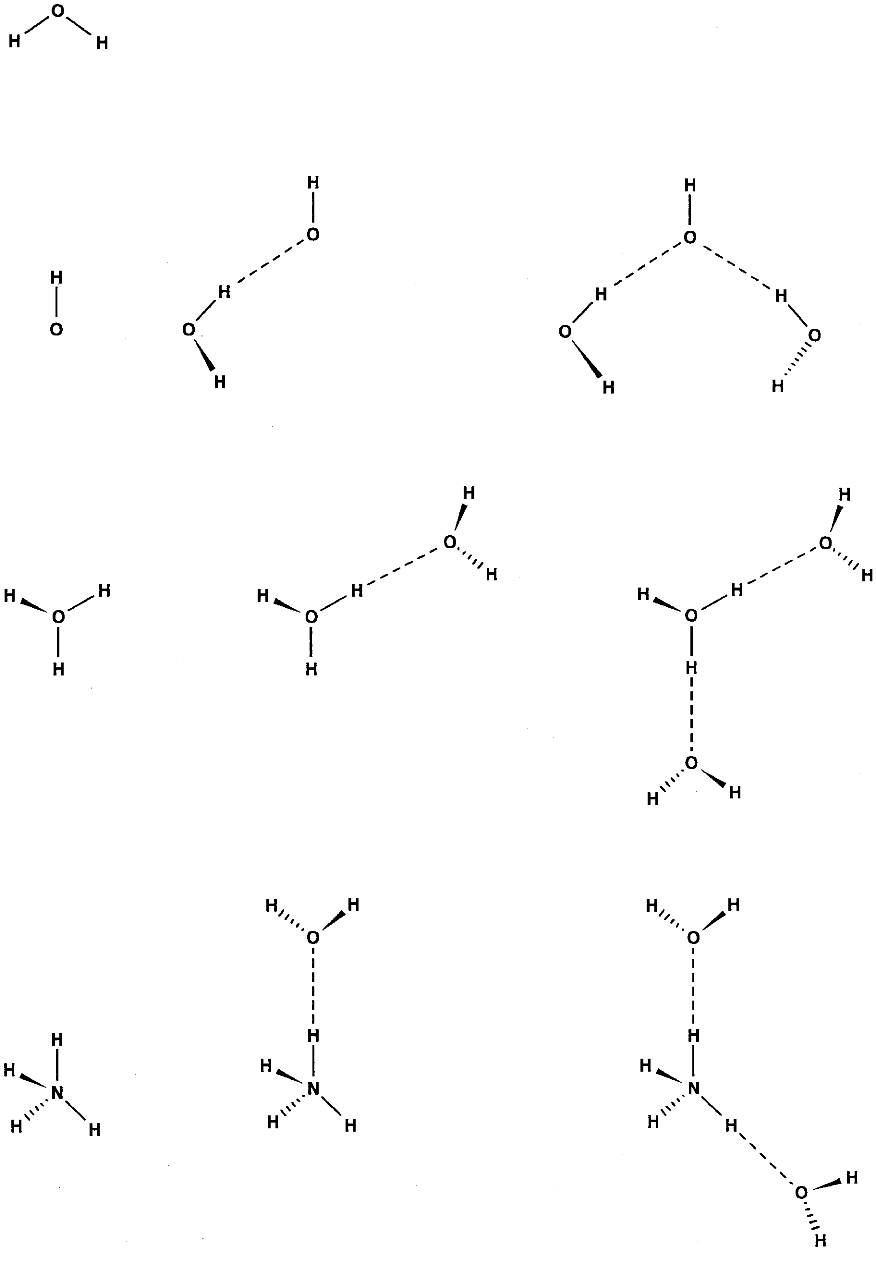

**Fig. 1.** The structures of $H_2O$, $OH^-(H_2O)_n$ ($n$ = 0–2), $H_3O^+(H_2O)_n$ ($n$ = 0–2), and $NH_4^+(H_2O)_n$ ($n$ = 0–2)

**Table 1.** Intermolecular interaction energies ($-\Delta E_{n-1,n}$) of $OH^{-}(H_2O)_n$ (kcal/mol)

| Basis set | MP2 | MP4 | QCISD(T) | CCSD(T) | B3LYP |
|---|---|---|---|---|---|
| *n* = 1 | | | | | |
| aug-cc-pVDZ | 26.7 (24.6) | 26.1 (23.6) | 26.8 (24.6) | 26.9 (24.6) | 27.8 (27.1) |
| aug-cc-pVTZ | 27.1 (25.9) | 26.5 (25.1) | 27.3 (26.1) | 27.4 (26.2) | 27.6 (27.1) |
| aug-cc-pVQZ | 26.9 (26.1) | 26.2 (25.5) | 27.1 (26.4) | 27.1 (26.5) | 27.4 (27.0) |
| aug-cc-pV5Z | 26.7 (26.3) | | | | 27.0 (26.8) |
| aug-cc-pV6Z | 26.6 (26.4) | | | | 26.8 (26.8) |
| CBS limit | 26.5 (26.4) | 25.7 (25.8) | 26.7 (26.5) | 26.6 (26.6) | 26.7 (26.7) |
| 6-311 + + G(d,p) | 28.3 (23.9) | 27.8 (22.9) | 28.2 (23.6) | 28.2 (23.7) | 29.4 (27.8) |
| 6-311 + + G(2d,2p) | 28.3 (24.8) | 28.0 (23.9) | 28.3 (24.6) | 28.3 (24.7) | 28.9 (27.4) |
| 6-311 + + G(3d,3p) | 27.9 (25.0) | 27.6 (24.2) | 28.0 (24.9) | 28.0 (25.0) | 28.9 (27.4) |
| 6-311 + + G(3df,3pd) | 28.6 (25.8) | 28.3 (25.2) | 28.7 (25.9) | 28.7 (25.9) | 29.1 (27.7) |
| *n* = 2 | | | | | |
| aug-cc-pVDZ | 22.0 (20.3) | 21.9 (20.0) | | 22.2 (20.4) | 21.8 (21.4) |
| aug-cc-pVTZ | 22.0 (21.1) | | | | 21.5 (21.4) |
| aug-cc-pVQZ | 21.9 (21.4) | | | | 21.3 (21.2) |
| aug-cc-pV5Z | 21.8 (21.3) | | | | 21.2 (21.2) |
| CBS limit | 21.7 (21.4) | | | | 21.1 (21.1) |
| 6-311 + + G(d,p) | 23.6 (20.1) | 23.6 (19.7) | | | 23.3 (22.2) |
| 6-311 + + G(2d,2p) | 22.4 (20.1) | 22.4 (19.8) | | | 22.0 (21.2) |
| 6-311 + + G(3d,3p) | 22.2 (20.2) | 22.2 (20.0) | | | 22.0 (21.3) |
| 6-311 + + G(3df,3pd) | 22.4 (20.6) | 22.4 (20.5) | | | 22.0 (21.4) |

**Table 2.** Basis set superposition error (*BSSE*) values for $OH^{-}$ $(H_2O)_n$ (kcal/mol)

| Basis set | MP2 | MP4 | QCISD(T) | CCSD(T) | B3LYP |
|---|---|---|---|---|---|
| *n* = 1 | | | | | |
| aug-cc-pVDZ | 2.1 | 2.5 | 2.3 | 2.3 | 0.7 |
| aug-cc-pVTZ | 1.2 | 1.4 | 1.2 | 1.2 | 0.5 |
| aug-cc-pVQZ | 0.8 | 0.7 | 0.6 | 0.6 | 0.4 |
| aug-cc-pV5Z | 0.4 | | | | 0.2 |
| aug-cc-pV6Z | 0.2 | | | | 0.1 |
| CBS limit | 0.1 | −0.1 | 0.2 | 0.0 | 0.0 |
| 6-311+ + G(d,p) | 4.4 | 5.0 | 4.6 | 4.6 | 1.6 |
| 6-311+ + G(2d,2p) | 3.4 | 4.1 | 3.7 | 3.7 | 1.5 |
| 6-311+ + G(3d,3p) | 2.9 | 3.4 | 3.0 | 3.0 | 1.5 |
| 6-311+ + G(3df,3pd) | 2.8 | 3.2 | 2.8 | 2.7 | 1.3 |
| *n* = 2 | | | | | |
| aug-cc-pVDZ | 1.7 | 1.9 | | | 0.4 |
| aug-cc-pVTZ | 0.9 | | | | 0.1 |
| aug-cc-pVQZ | 0.5 | | | | 0.1 |
| aug-cc-pV5Z | 0.5 | | | | 0.0 |
| CBS limit | 0.3 | | | | 0.0 |
| 6-311+ + G(d,p) | 3.5 | 3.9 | | | 1.2 |
| 6-311+ + G(2d,2p) | 2.2 | 2.6 | | | 0.8 |
| 6-311+ + G(3d,3p) | 2.0 | 2.2 | | | 0.7 |
| 6-311+ + G(3df,3pd) | 1.8 | 2.0 | | | 0.7 |

smaller, the counterpoise-uncorrected intermolecular interaction energies are closer to the CBS limit than are the counterpoise-corrected intermolecular interaction energies at each level (Fig. 2). The counterpoise-uncorrected intermolecular interaction energies evaluated using the MP2/aug-cc-pVDZ level are close to the CBS limit at the MP2, QCISD(T), and CCSD(T) levels (Fig. 3).

The trend for the intermolecular interaction energies of $OH^{-}(H_2O)$ calculated using the B3LYP/aug-cc-pV*x*Z ($x = D,T,Q,5,6$) level (Fig. 4) is extremely different from that calculated using the aug-cc-pV*x*Z ($x = D,T,Q,5,6$) basis sets at the MP2, MP4, QCISD(T), and CCSD(T) levels (Fig. 2): the BSSE is nearly zero in the CBS limit (Fig. 4). In addition, the counterpoise-uncorrected intermolecular interaction energies are nearly equal to the counterpoise-corrected intermolecular interaction energies in the CBS limit (Fig. 4); however, in contrast to the situation at the MP2, MP4, QCISD(T), and CCSD(T) levels, when the basis set is smaller, the counterpoise-corrected intermolecular interaction energies are closer to the CBS limit than are the counterpoise-uncorrected intermolecular interaction energies (Fig. 4). The CBS limit at the B3LYP level agrees with that at the MP2, QCISD(T), and CCSD(T) levels (Fig. 4).

For the intermolecular interaction energy of $OH^{-}(H_2O)$ calculated using the 6-311++G(d,p), 6-311++G(2d,2p), 6-311++G(3d,3p), and 6-311++

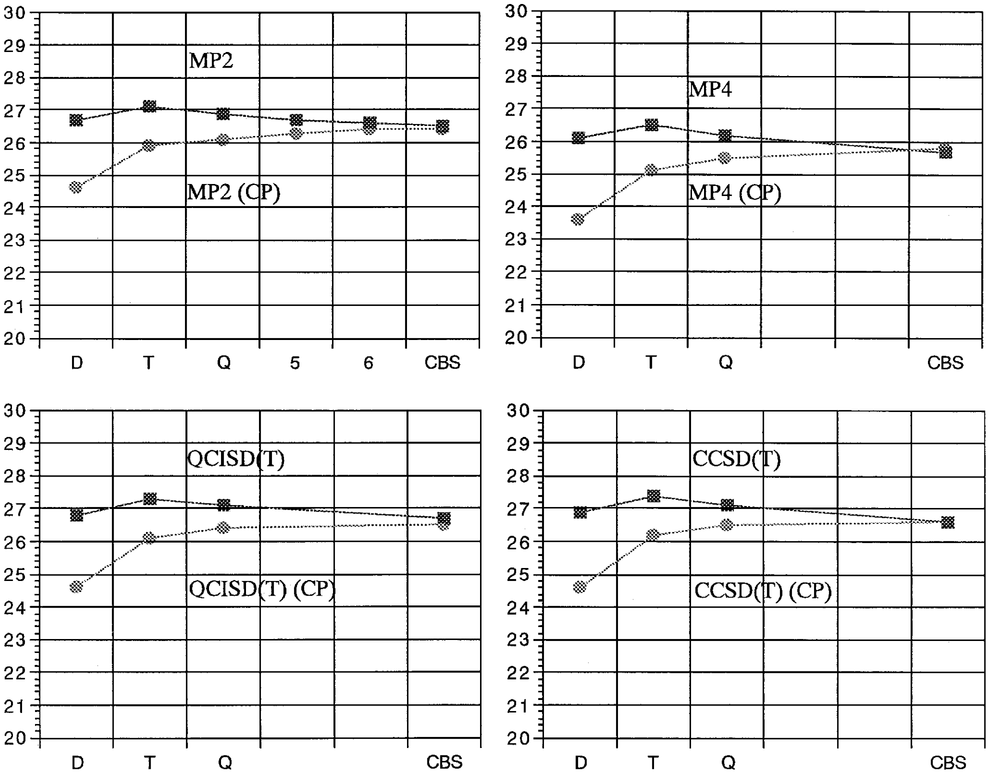

**Fig. 2.** Calculated intermolecular interaction energies of $OH^{-}(H_2O)$ as a function of the correlation-consistent basis set used. The counterpoise-corrected values are denoted by *CP*

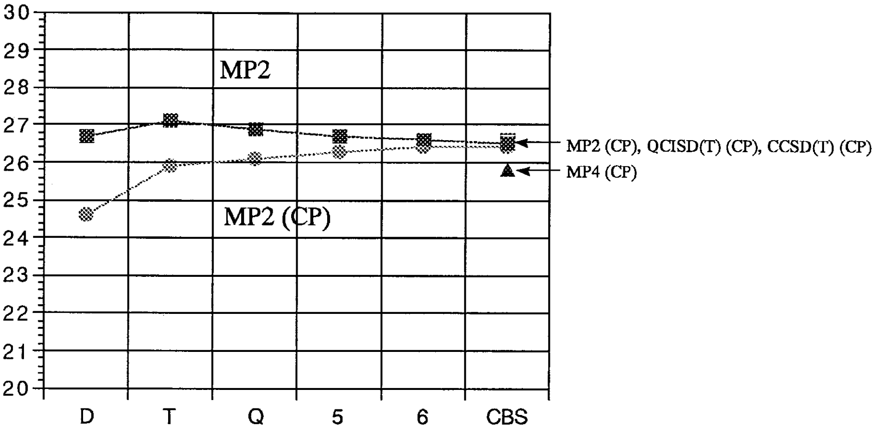

**Fig. 3.** The counterpoise-uncorrected intermolecular interaction energy of $OH^{-}(H_2O)$ evaluated using the MP2/aug-cc-pVDZ level is close to the complete basis set (*CBS*) limit at the MP2, QCISD(T), and CCSD(T) levels

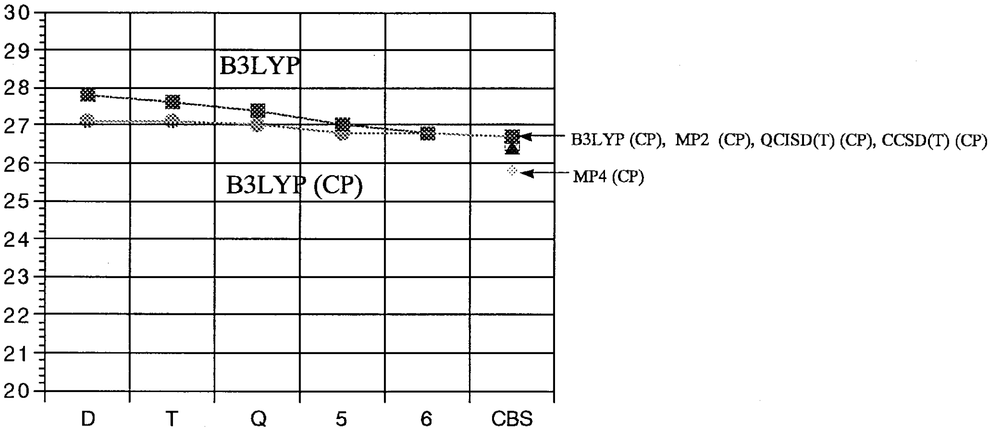

**Fig. 4.** Calculated intermolecular interaction energies of $OH^{-}(H_2O)$ as a function of the correlation-consistent basis set used. The counterpoise-corrected values are denoted by *CP*

G(3df,3pd) basis sets at the MP2, MP4, QCISD(T), CCSD(T), and B3LYP levels, when the basis sets are larger, the BSSE is smaller; however, BSSE is significant even for the 6-311+ +G(3df,3pd) basis set at all levels.

For the intermolecular interaction energy of $OH^-(H_2O)_2$ calculated at the MP2/aug-cc-pV$x$Z ($x$ = D,T,Q,5) level, the BSSE is nearly zero in the CBS limit (Fig. 5). In addition, the counterpoise-uncorrected intermolecular interaction energies are nearly equal to the counterpoise-corrected intermolecular interaction energies in the CBS limit (Fig. 5). When the basis set is smaller, the counterpoise-uncorrected intermolecular interaction energies are closer to the CBS limit than are the counterpoise-corrected intermolecular interaction energies (Fig. 5). The counterpoise-uncorrected intermolecular interaction energy evaluated using the MP2/aug-cc-pVDZ level is close to the CBS limit (Fig. 5).

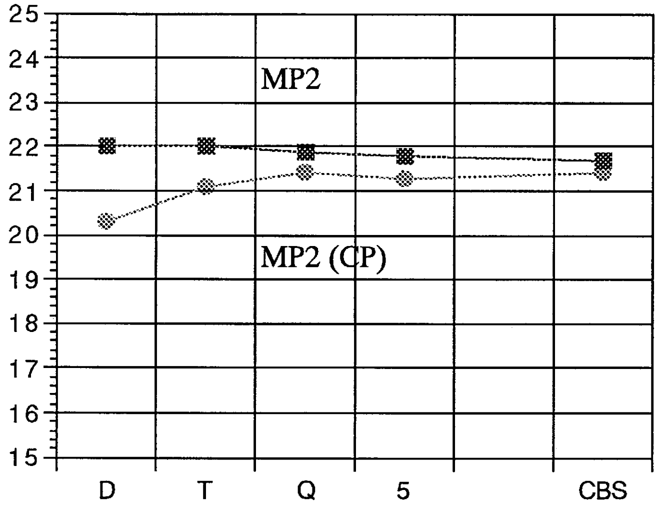

**Fig. 5.** Calculated intermolecular interaction energies of $OH^-(H_2O)_2$ as a function of the correlation-consistent basis set used. The counterpoise-corrected values are denoted by *CP*

The trend for the intermolecular interaction energies of $OH^-(H_2O)_2$ calculated using the B3LYP/aug-cc-pV$x$Z ($x$ = D,T,Q,5) level (Fig. 6) is very different from that calculated using the MP2/aug-cc-pV$x$Z ($x$ = D, T,Q,5) level (Fig. 5): the BSSE is nearly zero in the CBS limit (Fig. 6). In addition, the counterpoise-uncorrected intermolecular interaction energies are nearly equal to the counterpoise-corrected intermolecular interaction energies in the CBS limit (Fig. 6); however, in contrast to the situation at the MP2 level, when the basis set is smaller, the counterpoise-corrected intermolecular interaction energies are closer to the CBS limit than are the counterpoise-uncorrected intermolecular interaction energies (Fig. 6). The CBS limit at the B3LYP level is close to that at the MP2 level (Fig. 6).

For the intermolecular interaction energy of $OH^-(H_2O)_2$ calculated using the 6-311+ +G(d,p), 6-311+ +G(2d,2p), 6-311+ +G(3d,3p), and 6-311+ + G(3df,3pd) basis sets at the MP2, MP4, and B3LYP levels, when the basis sets are larger, the BSSE is smaller; however, the BSSE is significant even for the 6-311+ +G(3df,3pd) basis set at all levels.

### *3.2 $F^-(H_2O)$ and $Cl^-(H_2O)$*

The counterpoise-uncorrected and counterpoise-corrected intermolecular interaction energies and the BSSE for $F^-(H_2O)$ evaluated using the MP2/aug-cc-pV$x$Z ($x$ = D,T,Q,5) and CCSD(T)/aug-cc-pVxZ ($x$ = D,T,Q) levels [27] are shown in Tables 3 and 4. The BSSE is nearly zero in the CBS limit (Fig. 7). In addition, the counterpoise-uncorrected intermolecular interaction energies are nearly equal to the counterpoise-corrected intermolecular interaction energies in the CBS limit (Fig. 7). When the basis set is smaller, the counterpoise-uncorrected intermolecular interaction energies are closer to the CBS limit than the counterpoise-corrected intermolecular interaction energies at each level (Fig. 7). The counterpoise-uncorrected intermolecular interaction

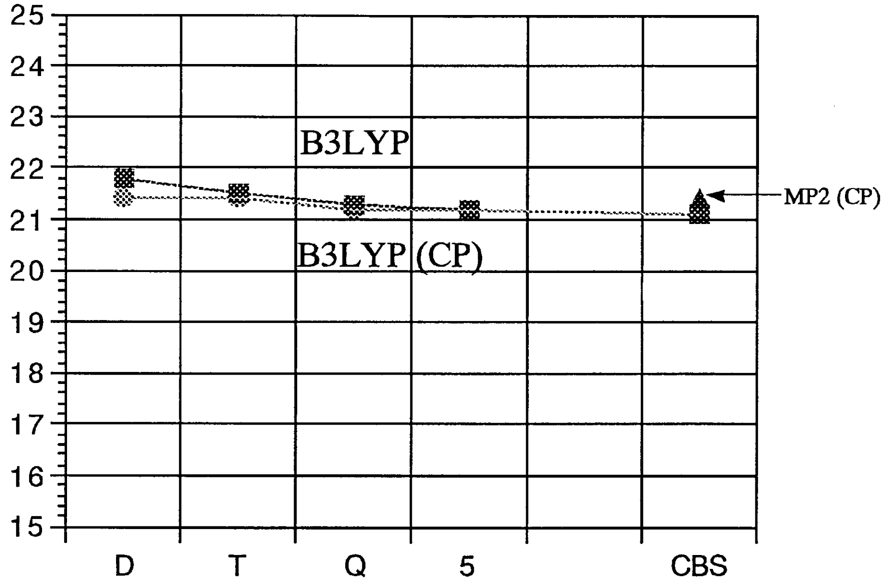

**Fig. 6.** Calculated intermolecular interaction energies of $OH^-(H_2O)_2$ as a function of the correlation-consistent basis set used. The counterpoise-corrected values are denoted by *CP*

energy evaluated using the MP2/aug-cc-pVDZ level is close to the CBS limit at the MP2 and CCSD(T) levels (Fig. 8).

**Table 3.** Intermolecular interaction energies ($-\Delta E_{n-1,n}$) of $F^-(H_2O)$ (kcal/mol) based on the data of Weis et al. [27]

| Basis set | MP2 | CCSD(T) |
|---|---|---|
| aug-cc-pVDZ | 26.8 (25.3) | 27.1 (25.4) |
| aug-cc-pVTZ | 27.6 (26.5) | 27.8 (26.7) |
| aug-cc-pVQZ | 27.5 (26.7) | 27.6 (27.0) |
| aug-cc-pV5Z | 27.3 (26.9) | |
| CBS limit | 27.1 (26.9) | 27.2 (27.2) |

**Table 4.** BSSE values for $F^-(H_2O)$ (kcal/mol) based on the data of Weis et al. [27]

| Basis set | MP2 | CCSD(T) |
|---|---|---|
| aug-cc-pVDZ | 1.5 | 1.7 |
| aug-cc-pVTZ | 1.1 | 1.1 |
| aug-cc-pVQZ | 0.8 | 0.6 |
| aug-cc-pV5Z | 0.4 | |
| CBS limit | 0.1 | 0.0 |

For the intermolecular interaction energy of $Cl^-(H_2O)$ calculated using the MP2/aug-cc-pV$x$Z ($x$ = D,T,Q,5) level [26], similar results are found.

### 3.3 $H_3O^+(H_2O)_n$

The counterpoise-uncorrected and counterpoise-corrected intermolecular interaction energies and the BSSE for $H_3O^+(H_2O)_n$ ($n = 1,2$) evaluated using the aug-cc-pV$x$Z ($x$ = D,T,Q,5,6), 6-311++G(d,p), 6-311+G(2d,2p), 6-311++G(3d,3p), and 6-311++G(3df,3pd) basis sets at the MP2, MP4, QCISD(T), CCSD(T), and B3LYP levels are shown in Tables 5 and 6.

For the intermolecular interaction energy of $H_3O^+(H_2O)$ calculated using the aug-cc-pV$x$Z ($x$ = D,T,Q,5,6) basis sets at the MP2 and MP4 levels, the BSSE is nearly zero in the CBS limit (Fig. 9). In addition, the counterpoise-uncorrected intermolecular interaction energies are nearly equal to the counterpoise-

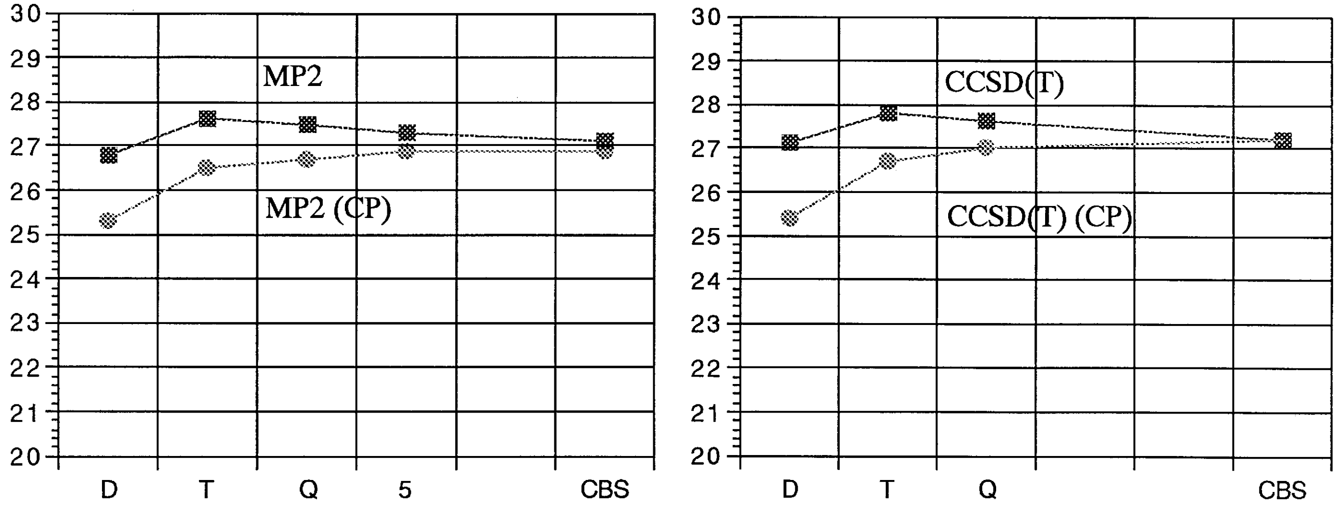

**Fig. 7.** Calculated intermolecular interaction energies of $F^-(H_2O)$ as a function of the correlation-consistent basis set used. The counterpoise-corrected values are denoted by *CP*. Based on the data of Weis et al. [27]

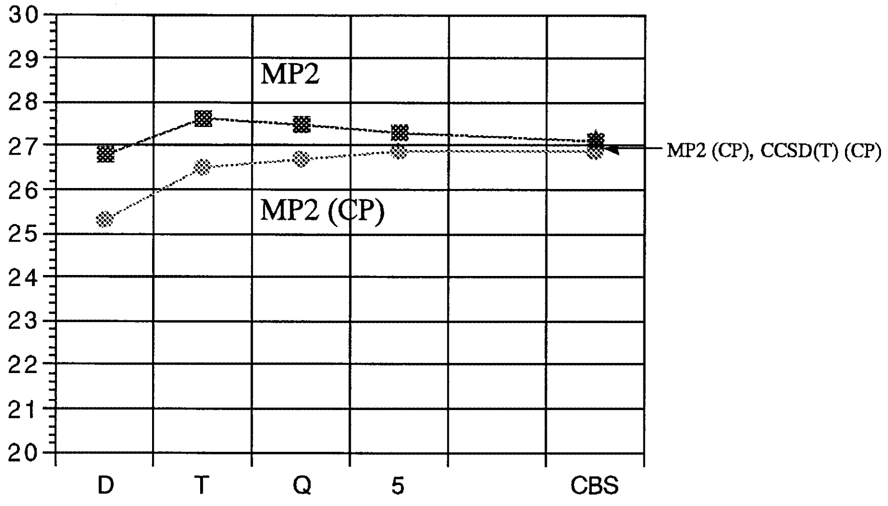

**Fig. 8.** The counterpoise-uncorrected intermolecular interaction energy of $F^-(H_2O)$ evaluated using the MP2/aug-cc-pVDZ level is close to the CBS limit at the MP2 and CCSD(T) levels

corrected intermolecular interaction energies in the CBS limit (Fig. 9). When the basis set is smaller, the counterpoise-uncorrected intermolecular interaction energies are closer to the CBS limit than the counterpoise-corrected intermolecular interaction energies at each level (Fig. 9). The counterpoise-uncorrected intermolecular interaction energy evaluated using the MP2/aug-cc-pVDZ level is close to the CBS limit at the MP2 and MP4 levels (Fig. 10).

The trend for the intermolecular interaction energies of $H_3O^+(H_2O)$ calculated using the B3LYP/aug-cc-pV$x$Z ($x = $ D,T,Q,5) level (Fig. 11) is extremely different from that calculated using the aug-cc-pV$x$Z ($x = $ D,T,Q,5,6) basis sets at the MP2 and MP4 levels (Fig. 9): the BSSE is nearly zero in the CBS limit (Fig. 11). In addition, the counterpoise-uncorrected intermolecular interaction energies are nearly equal to the counterpoise-corrected intermolecular interaction energies in the CBS limit (Fig. 11). The CBS limit at the B3LYP level disagrees with that at the MP2 and MP4 levels (Fig. 11).

For the intermolecular interaction energy of $H_3O^+(H_2O)$ calculated using the 6-311 + + G(d,p), 6-311 + + G(2d,2p), 6-311 + + G(3d,3p), and 6-311 + + G(3df,3pd) basis sets at the MP2, MP4, QCISD(T), CCSD(T), and B3LYP levels, when the basis sets are larger, the BSSE is smaller; however, the BSSE is significant even for the 6-311 + + G(3df,3pd) basis set at all levels except for the B3LYP level. At the B3LYP level, the BSSE is negligible for the 6-311 + + G(3df,3pd) basis set.

**Table 5.** Intermolecular interaction energies ($-\Delta E_{n-1,n}$) of $H_3O^+(H_2O)_n$ (kcal/mol)

| Basis set | MP2 | MP4 | QCISD(T) | CCSD(T) | B3LYP |
|---|---|---|---|---|---|
| $n = 1$ | | | | | |
| aug-cc-pVDZ | 34.1 (31.8) | 33.5 (31.1) | 33.5 (31.1) | 33.5 (31.1) | 35.4 (34.8) |
| aug-cc-pVTZ | 34.5 (33.3) | 34.1 (32.9) | 34.1 (32.9) | 34.1 (32.9) | 35.1 (35.0) |
| aug-cc-pVQZ | 34.4 (33.7) | 33.9 (33.4) | | | 35.6 (35.5) |
| aug-cc-pV5Z | 34.3 (33.9) | | | | 35.5 (35.5) |
| aug-cc-pV6Z | 34.3 (34.1) | | | | |
| CBS limit | 34.2 (34.1) | 33.5 (33.8) | | | 35.8 (35.8) |
| 6-311 + + G(d,p) | 35.5 (31.5) | 35.0 (30.7) | 34.9 (30.7) | 34.9 (30.7) | 36.7 (35.2) |
| 6-311 + + G(2d,2p) | 33.9 (31.5) | 33.3 (30.7) | 33.3 (30.7) | 33.3 (30.7) | 35.3 (34.5) |
| 6-311 + + G(3d,3p) | 34.3 (31.8) | 33.9 (31.2) | 33.8 (31.2) | 33.8 (31.2) | 35.1 (34.7) |
| 6-311 + + G(3df,3pd) | 34.8 (32.9) | 34.4 (32.4) | 34.4 (32.4) | 34.4 (32.4) | 35.5 (35.2) |
| $n = 2$ | | | | | |
| aug-cc-pVDZ | 23.8 (22.0) | | | | 23.4 (22.9) |
| aug-cc-pVTZ | 23.6 (22.8) | | | | 23.0 (22.9) |
| aug-cc-pVQZ | 23.6 (23.1) | | | | 23.2 (23.1) |
| aug-cc-pV5Z | 23.5 (23.3) | | | | 23.1 (23.1) |
| CBS limit | 23.5 (23.5) | | | | 23.3 (23.2) |
| 6-311 + + G(d,p) | 24.7 (21.9) | | | | 24.7 (23.5) |
| 6-311 + + G(2d,2p) | 23.7 (22.0) | | | | 23.3 (22.7) |
| 6-311 + + G(3d,3p) | 23.6 (21.9) | | | | 23.2 (22.8) |
| 6-311 + + G(3df,3pd) | 23.8 (22.4) | | | | 23.4 (23.0) |

**Table 6.** BSSE values for $H_3O^+(H_2O)_n$ (kcal/mol)

| Basis set | MP2 | MP4 | QCISD(T) | CCSD(T) | B3LYP |
|---|---|---|---|---|---|
| $n = 1$ | | | | | |
| aug-cc-pVDZ | 2.3 | 2.5 | 2.4 | 2.4 | 0.5 |
| aug-cc-pVTZ | 1.2 | 1.2 | 1.2 | 1.2 | 0.1 |
| aug-cc-pVQZ | 0.7 | 0.6 | | | 0.1 |
| aug-cc-pV5Z | 0.4 | | | | 0.0 |
| aug-cc-pV6Z | 0.2 | | | | |
| CBS limit | 0.1 | −0.3 | | | 0.0 |
| 6-311 + + G(d,p) | 4.0 | 4.3 | 4.2 | 4.2 | 1.5 |
| 6-311 + + G(2d,2p) | 2.4 | 2.6 | 2.6 | 2.5 | 0.8 |
| 6-311 + + G(3d,3p) | 2.5 | 2.7 | 2.7 | 2.6 | 0.4 |
| 6-311 + + G(3df,3pd) | 2.0 | 2.0 | 2.0 | 2.0 | 0.3 |
| $n = 2$ | | | | | |
| aug-cc-pVDZ | 1.8 | | | | 0.5 |
| aug-cc-pVTZ | 0.8 | | | | 0.1 |
| aug-cc-pVQZ | 0.5 | | | | 0.1 |
| aug-cc-pV5Z | 0.2 | | | | 0.0 |
| CBS limit | 0.0 | | | | 0.0 |
| 6-311 + + G(d,p) | 2.8 | | | | 1.1 |
| 6-311 + + G(2d,2p) | 1.7 | | | | 0.6 |
| 6-311 + + G(3d,3p) | 1.7 | | | | 0.3 |
| 6-311 + + G(3df,3pd) | 1.4 | | | | 0.4 |

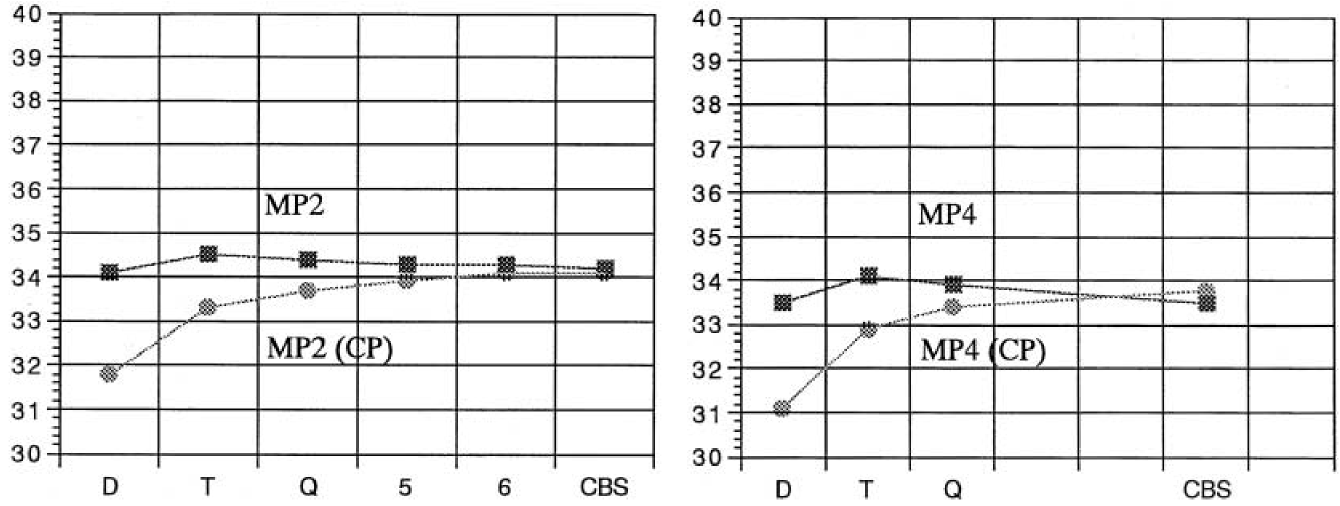

**Fig. 9.** Calculated intermolecular interaction energies of $H_3O^+(H_2O)$ as a function of the correlation-consistent basis set used. The counterpoise-corrected values are denoted by *CP*

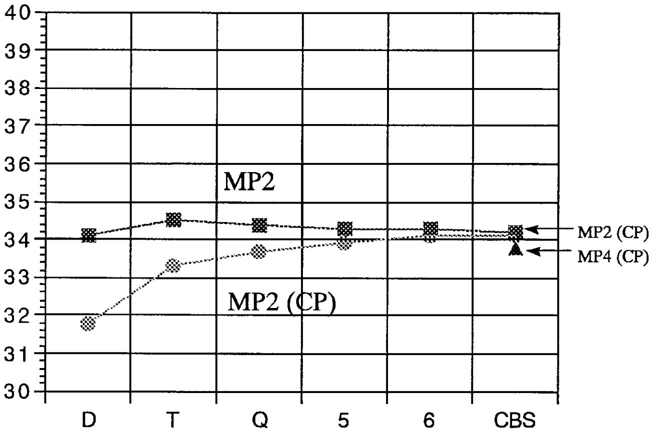

**Fig. 10.** The counterpoise-uncorrected intermolecular interaction energy of $H_3O^+(H_2O)$ evaluated using the MP2/aug-cc-pVDZ level is close to the CBS limit at the MP2 and MP4 levels

For the intermolecular interaction energy of $H_3O^+(H_2O)_2$ calculated using MP2/aug-cc-pV$x$Z ($x$ = D,T,Q,5) level, the BSSE is nearly zero in the CBS limit (Fig. 12). In addition, the counterpoise-uncorrected intermolecular interaction energies are nearly equal to the counterpoise-corrected intermolecular interaction energies in the CBS limit (Fig. 12). When the basis set is smaller, the counterpoise-uncorrected intermolecular interaction energies are closer to the CBS limit than the counterpoise-corrected intermolecular interaction energies (Fig. 12). The counterpoise-uncorrected intermolecular interaction energy evaluated using the MP2/aug-cc-pVDZ level is close to the CBS limit (Fig. 12).

The trend for the intermolecular interaction energies of $H_3O^+(H_2O)_2$ calculated using the B3LYP/aug-cc-pV$x$Z ($x$ = D,T,Q,5) level (Fig. 13) is extremely different from that calculated using the MP2/aug-cc-pV$x$Z ($x$ = D,T,Q,5) level (Fig. 12): the BSSE is nearly zero in the CBS limit (Fig. 13). In addition, the counterpoise-uncorrected intermolecular interaction energies are nearly equal to the counterpoise-corrected intermolecular interaction energies in the CBS limit (Fig. 13). The

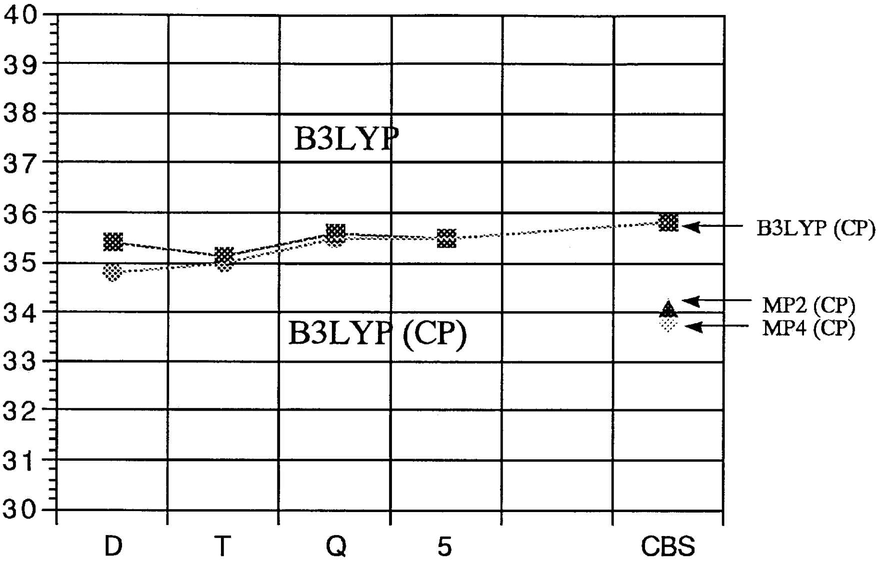

**Fig. 11.** Calculated intermolecular interaction energies of $H_3O^+(H_2O)$ as a function of the correlation-consistent basis set used. The counterpoise-corrected values are denoted by *CP*

CBS limit at the B3LYP level is close to that at the MP2 level (Fig. 13).

For the intermolecular interaction energy of $H_3O^+(H_2O)_2$ calculated using the 6-311++G(d,p), 6-311++G(2d,2p), 6-311++G(3d,3p), and 6-311++G(3df,3pd) basis sets at the MP2 and B3LYP levels, when the basis sets are larger, the BSSE is smaller; however, at the MP2 level, the BSSE is significant even for the 6-311++G(3df,3pd) basis set. At the B3LYP level, the BSSE is negligible for the 6-311++G(3d,3p) and 6-311++G(3df,3pd) basis sets.

### 3.4 $NH_4^+(H_2O)_n$

The counterpoise-uncorrected and counterpoise-corrected intermolecular interaction energies and the BSSE for $NH_4^+(H_2O)_n$ ($n = 1,2$) evaluated using the aug-cc-pV*x*Z ($x = $ D,T,Q,5), 6-311++G(d,p), 6-311++G(2d,2p), 6-311++G(3d,3p), and 6-311++G(3df,3pd) basis sets at the MP2, MP4, QCISD(T), CCSD(T), and B3LYP levels are shown in Tables 7 and 8.

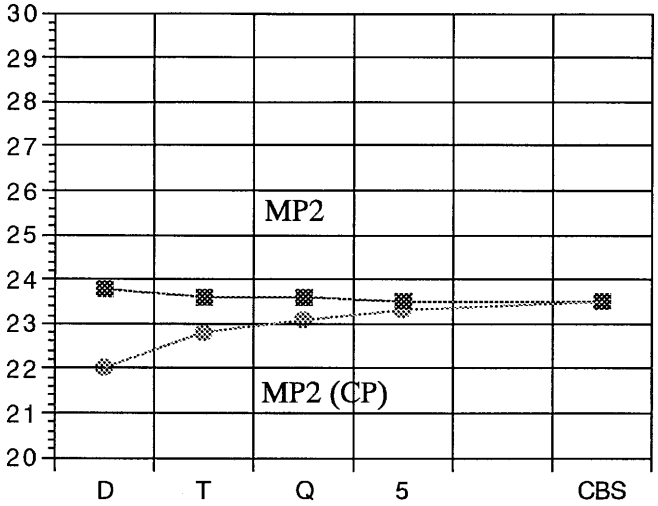

**Fig. 12.** Calculated intermolecular interaction energies of $H_3O^+(H_2O)_2$ as a function of the correlation-consistent basis set used. The counterpoise-corrected values are denoted by *CP*

For the intermolecular interaction energy of $NH_4^+(H_2O)$ calculated using the aug-cc-pV*x*Z ($x = $ D,T,Q,5) basis sets at the MP2 and MP4 levels, the BSSE is nearly zero in the CBS limit (Fig. 14). In addition, the counterpoise-uncorrected intermolecular interaction energies are nearly equal to the counterpoise-corrected intermolecular interaction energies in the CBS limit (Fig. 14). When the basis set is smaller, the counterpoise-uncorrected intermolecular interaction energies are closer to the CBS limit than the counterpoise-corrected intermolecular interaction energies at each level (Fig. 14). The counterpoise-uncorrected intermolecular interaction energy evaluated using the MP2/aug-cc-pVDZ level is close to the CBS limit at the MP2 and MP4 levels (Fig. 15).

The trend for the intermolecular interaction energies of $NH_4^+(H_2O)$ calculated using the B3LYP/aug-cc-pV*x*Z ($x = $ D,T,Q,5) level (Fig. 16) is extremely different from that calculated using the aug-cc-pV*x*Z ($x = $ D,T,Q,5) basis sets at the MP2 and MP4 levels (Fig. 14): the BSSE is nearly zero in the CBS limit (Fig. 16). In addition, the counterpoise-uncorrected intermolecular interaction energies are nearly equal to the counterpoise-corrected intermolecular interaction energies in the CBS limit (Fig. 16). The CBS limit at the B3LYP level agrees with that at the MP2 and MP4 levels (Fig. 16).

For the intermolecular interaction energy of $NH_4^+(H_2O)$ calculated using the 6-311++G(d,p), 6-311++G(2d,2p), 6-311++G(3d,3p), and 6-311++G(3df,3pd) basis sets at the MP2, MP4, QCISD(T), CCSD(T), and B3LYP levels, when the basis sets are larger, the BSSE is smaller: however, the BSSE is significant even for the 6-311++G(3df,3pd) basis set at all levels except for the B3LYP level. At the B3LYP level, the BSSE is negligible for the 6-311++G(2d,2p), 6-311++G(3d,3p), and 6-311++G(3df,3pd) basis sets.

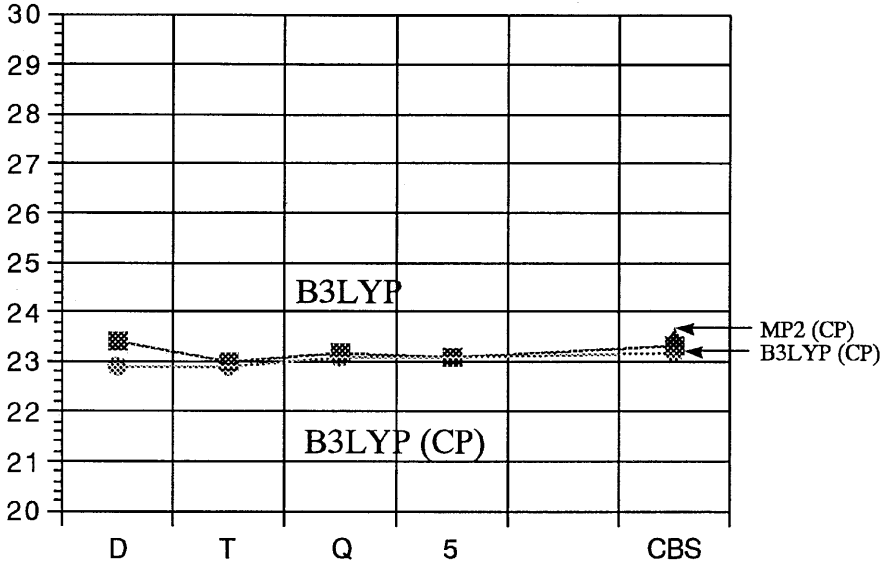

**Fig. 13.** Calculated intermolecular interaction energies of $H_3O^+(H_2O)_2$ as a function of the correlation-consistent basis set used. The counterpoise-corrected values are denoted by *CP*

**Table 7.** Intermolecular interaction energies ($-\Delta E_{n-1,n}$) of $NH_4^+(H_2O)_n$ (kcal/mol)

| Basis set | MP2 | MP4 | QCISD(T) | CCSD(T) | B3LYP |
|---|---|---|---|---|---|
| $n = 1$ | | | | | |
| aug-cc-pVDZ | 20.7 (19.3) | 20.5 (19.0) | 20.5 (19.0) | 20.5 (19.1) | 20.9 (20.2) |
| aug-cc-pVTZ | 20.7 (20.1) | 20.5 (19.9) | 20.5 (20.0) | 20.5 (20.0) | 20.4 (20.3) |
| aug-cc-pVQZ | 20.7 (20.4) | 20.5 (20.2) | | | 20.5 (20.5) |
| aug-cc-pV5Z | 20.6 (20.4) | | | | 20.5 (20.5) |
| CBS limit | 20.6 (20.5) | 20.5 (20.4) | | | 20.6 (20.6) |
| 6-311++G(d,p) | 21.6 (19.7) | 21.3 (19.3) | 21.3 (19.3) | 21.3 (19.4) | 22.0 (21.1) |
| 6-311++G(2d,2p) | 20.5 (19.4) | 20.3 (19.1) | 20.3 (19.1) | 20.3 (19.1) | 20.6 (20.2) |
| 6-311++G(3d,3p) | 20.6 (19.4) | 20.4 (19.2) | 20.4 (19.2) | 20.4 (19.2) | 20.5 (20.3) |
| 6-311++G(3df,3pd) | 20.9 (19.9) | 20.7 (19.7) | 20.7 (19.7) | 20.7 (19.7) | 20.7 (20.4) |
| $n = 2$ | | | | | |
| aug-cc-pVDZ | 17.4 (16.0) | | | | 17.0 (16.6) |
| aug-cc-pVTZ | 17.2 (16.7) | | | | 16.6 (16.5) |
| aug-cc-pVQZ | 17.2 (16.9) | | | | 16.7 (16.7) |
| aug-cc-pV5Z | | | | | 16.7 (16.7) |
| CBS limit | 17.2 (17.0) | | | | 16.8 (16.8) |
| 6-311++G(d,p) | 18.2 (16.4) | | | | 18.1 (17.3) |
| 6-311++G(2d,2p) | 17.3 (16.2) | | | | 16.7 (16.6) |
| 6-311++G(3d,3p) | 17.2 (16.2) | | | | 16.6 (16.5) |
| 6-311++G(3df,3pd) | 17.3 (16.4) | | | | 16.9 (16.6) |

**Table 8.** BSSE values for $NH_4^+(H_2O)_n$ (kcal/mol)

| Basis set | MP2 | MP4 | QCISD(T) | CCSD(T) | B3LYP |
|---|---|---|---|---|---|
| $n = 1$ | | | | | |
| aug-cc-pVDZ | 1.4 | 1.5 | 1.5 | 1.5 | 0.8 |
| aug-cc-pVTZ | 0.6 | 0.6 | 0.5 | 0.5 | 0.1 |
| aug-cc-pVQZ | 0.3 | 0.2 | | | 0.0 |
| aug-cc-pV5Z | 0.2 | | | | 0.0 |
| CBS limit | 0.1 | 0.1 | | | 0.0 |
| 6-311++G(d,p) | 1.9 | 2.0 | 2.0 | 1.9 | 0.8 |
| 6-311++G(2d,2p) | 1.2 | 1.3 | 1.2 | 1.2 | 0.3 |
| 6-311++G(3d,3p) | 1.1 | 1.2 | 1.2 | 1.2 | 0.2 |
| 6-311++G(3df,3pd) | 1.0 | 1.1 | 1.0 | 1.0 | 0.3 |
| $n = 2$ | | | | | |
| aug-cc-pVDZ | 1.3 | | | | 0.4 |
| aug-cc-pVTZ | 0.6 | | | | 0.1 |
| aug-cc-pVQZ | 0.3 | | | | 0.0 |
| aug-cc-pV5Z | | | | | 0.0 |
| CBS limit | 0.2 | | | | 0.0 |
| 6-311++G(d,p) | 1.5 | | | | 0.8 |
| 6-311++G(2d,2p) | 1.1 | | | | 0.1 |
| 6-311++G(3d,3p) | 1.1 | | | | 0.1 |
| 6-311++G(3df,3pd) | 0.9 | | | | 0.3 |

For the intermolecular interaction energy of $NH_4^+(H_2O)_2$ calculated at the MP2/aug-cc-pV$x$Z ($x$ = D,T,Q) level, the BSSE is nearly zero in the CBS limit (Fig. 17). In addition, the counterpoise-uncorrected intermolecular interaction energies are nearly equal to the counterpoise-corrected intermolecular interaction energies in the CBS limit (Fig. 17). When the basis set is smaller, the counterpoise-uncorrected intermolecular interaction energies are closer to the CBS limit than the counterpoise-corrected intermolecular interaction energies (Fig. 17). The counterpoise-uncorrected intermolecular interaction energy evaluated using the MP2/aug-cc-pVDZ level is close to the CBS limit (Fig. 17).

The trend for the intermolecular interaction energies of $NH_4^+(H_2O)_2$ calculated using the B3LYP/aug-cc-pV$x$Z ($x$ = D,T,Q,5) level (Fig. 18) is extremely different from that calculated using the MP2/aug-cc-pV$x$Z ($x$ = D,T,Q) levels (Fig. 17): the BSSE is nearly zero in the CBS limit (Fig. 18). In addition, the counterpoise-uncorrected intermolecular interaction energies are nearly equal to the counterpoise-corrected intermolecular interaction energies in the CBS limit (Fig. 18). The CBS limit at the B3LYP level agrees with that at the MP2 level (Fig. 18).

For the intermolecular interaction energy of $NH_4^+(H_2O)_2$ calculated using the 6-311++G(d,p), 6-311++G(2d,2p), 6-311++G(3d,3p), and 6-311++G(3df,3pd) basis sets at the MP2 and B3LYP levels, when the basis sets are larger, the BSSE is smaller; however, at the MP2 level, the BSSE is significant even for the 6-311++G(3df,3pd) basis set. At the B3LYP level, the BSSE is negligible for the 6-311++G(2d,2p), 6-311++G(3d,3p), and 6-311++G(3df,3pd) basis sets.

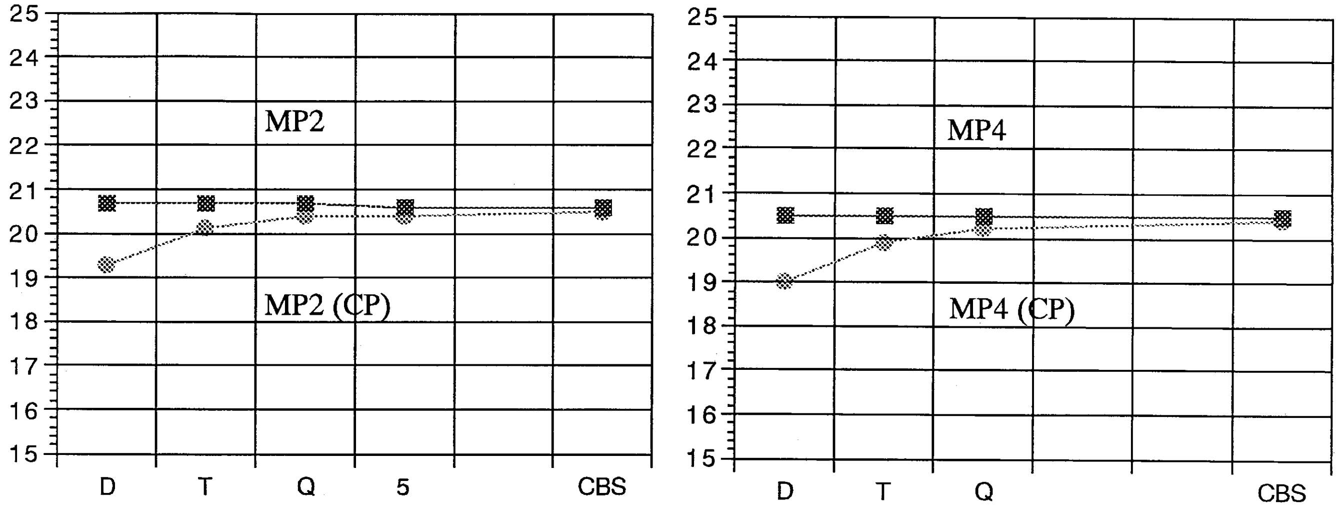

**Fig. 14.** Calculated intermolecular interaction energies of $NH_4^+(H_2O)$ as a function of the correlation-consistent basis set used. The counterpoise-corrected values are denoted by *CP*

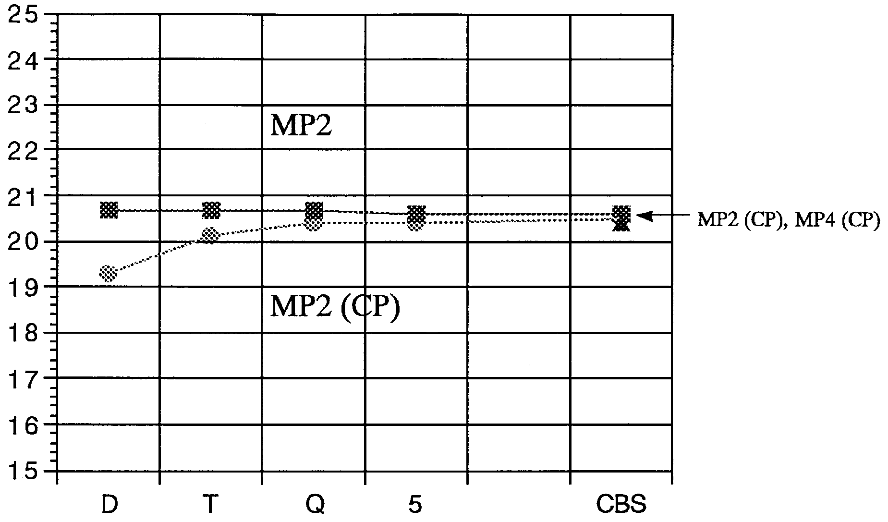

**Fig. 15.** The counterpoise-uncorrected intermolecular interaction energy of $NH_4^+(H_2O)$ evaluated using the MP2/aug-cc-pVDZ level is close to the CBS limit at the MP2 and MP4 levels

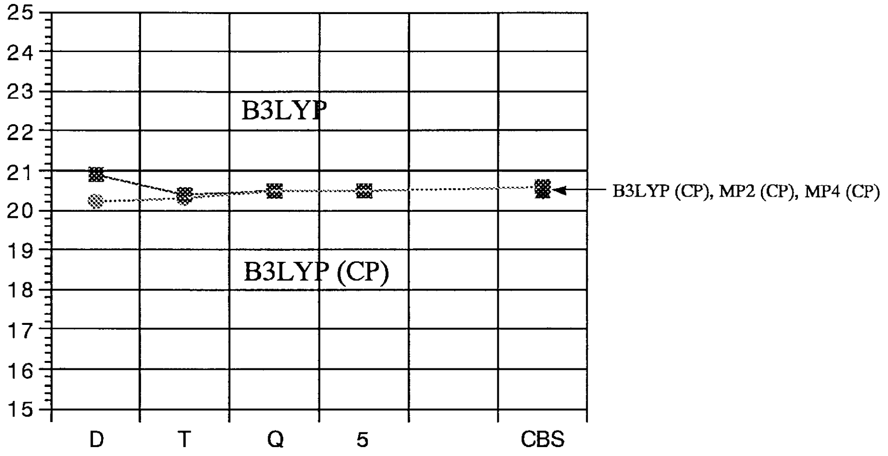

**Fig. 16.** Calculated intermolecular interaction energies of $NH_4^+(H_2O)$ as a function of the correlation-consistent basis set used. The counterpoise-corrected values are denoted by *CP*

## 4 Discussion

We discuss the results calculated with the correlation-consistent basis sets at the MP2, MP4, QCISD(T), and CCSD(T) levels.

The BSSE is not exactly equal to zero in the CBS limit because the CBS limit is not calculated using a CBS but is estimated by fitting from the intermolecular interaction energies calculated using the aug-cc-pV$x$Z basis sets ($x$ = D,T,Q,5,6) at each level.

When the basis set is smaller, because the counterpoise-uncorrected intermolecular interaction energies are closer to the CBS limit than the counterpoise-corrected intermolecular interaction energies at each level, the counterpoise-uncorrected intermolecular interaction energies are more reliable than the counterpoise-corrected intermolecular interaction energies.

Because the counterpoise-uncorrected intermolecular interaction energies evaluated using the MP2/aug-cc-pVDZ level are close to the CBS limit at the MP2, MP4, QCISD(T), and CCSD(T) levels, the counterpoise-uncorrected intermolecular interaction energies evaluated using the MP2/aug-cc-pVDZ level are reliable.

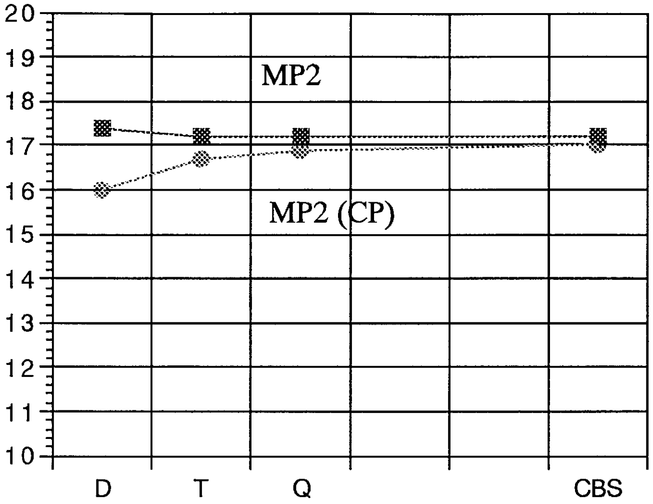

**Fig. 17.** Calculated intermolecular interaction energies of $NH_4^+(H_2O)_2$ as a function of the correlation-consistent basis set used. The counterpoise-corrected values are denoted by *CP*

Schwenke and Turhlar [28] advocated that for larger basis sets the counterpoise correction does not necessarily improve the result. Our results agree with this suggestion.

## 5 Conclusions

1. For the intermolecular interaction energies of ion-water clusters [$OH^-(H_2O)_n$ ($n$ = 1,2), $F^-(H_2O)$, $Cl^-(H_2O)$, $H_3O^+(H_2O)_n$ ($n$ = 1,2), and $NH_4^+(H_2O)_n$ ($n$ = 1,2)] calculated with correlation-consistent basis sets at the MP2, MP4, QCISD(T), and CCSD(T) levels, the BSSE is nearly zero in the CBS limit. That is, the counterpoise-uncorrected intermolecular interaction energies are nearly equal to the counterpoise-corrected intermolecular interaction energies in the CBS limit. When the basis set is smaller, the counterpoise-uncorrected intermolecular interaction energies are more reliable than the counterpoise-corrected intermolecular interaction energies. The counterpoise-uncorrected intermolecular interaction energies evaluated using the MP2/aug-cc-pVDZ level are reliable. These results are important because it is expected that these findings hold for other ion-water clusters.
2. The trend for the intermolecular interaction energies of the ion-water clusters calculated using the B3LYP/aug-cc-pV$x$Z ($x$ = D,T,Q,5,6) level is very different from that calculated using the aug-cc-pV$x$Z ($x$ = D,T,Q,5,6) basis sets at the MP2, MP4, QCISD(T), and CCSD(T) levels. For the intermolecular interaction energies of the ion-water clusters except for $H_3O^+(H_2O)$ calculated with correlation-consistent basis sets at the B3LYP level, the CBS limit is reliable.
3. In the 6-311++G(d,p), 6-311++G(2d,2p), 6-311++G(3d,3p), and 6-311++G(3df,3pd) basis sets, the BSSE is significant even for the 6-311++G(3df,3pd) basis set at the MP2, MP4, QCISD(T), and CCSD(T) levels. At the B3LYP level, the BSSE is negligible for the larger basis set, for example, the

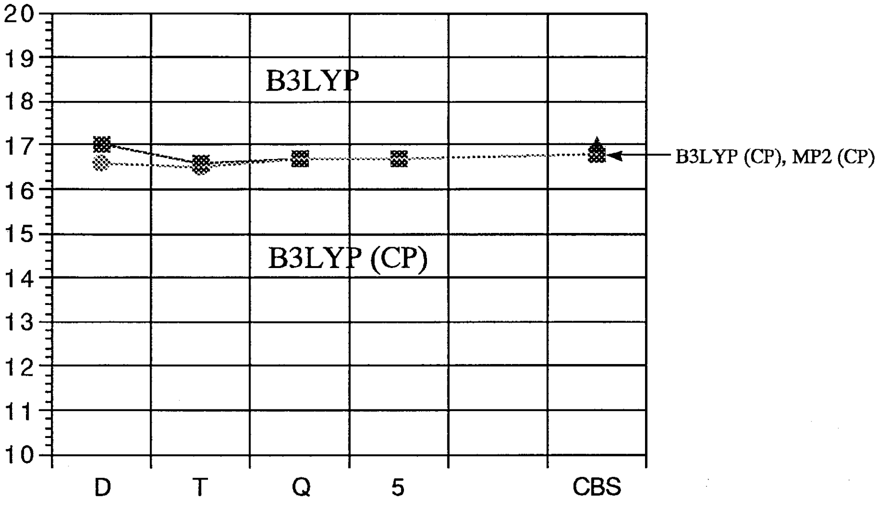

**Fig. 18.** Calculated intermolecular interaction energies of $NH_4^+(H_2O)_2$ as a function of the correlation-consistent basis set used. The counterpoise-corrected values are denoted by *CP*

6-311++G(3df,3pd) basis set, except for $OH^-(H_2O)_n$ ($n = 1,2$).

*Acknowledgements.* We are grateful to the Research Center for Computational Science for the use of computer time and the Gaussian 94, Gaussian 98 and Molpro 96 programs. We are grateful to Professor S.S. Xantheas and the American Chemical Society for permission to quote the results of $F^-(H_2O)$.

## References

1. Liu B, Mclean AD (1973) J Chem Phys 59: 4557
2. Boys SF, Bernardi F (1970) Mol Phys 19: 553
3. van Duijneveldt FB, van Duijneveldt JGCM, van Lenthe JH (1994) Chem Rev 94: 1873
4. van Mourik T, Wilson AK, Peterson KA, Woon DE, Dunning TH Jr (1999) Adv Quantum Chem 31: 105
5. Masamura M, Ikuta S (1999) J Comput Chem 20: 1138
6. Masamura M (2001) J Comput Chem 22: 31
7. Woon DE, Dunning TH Jr (1993) J Chem Phys 98: 1358
8. Kendall RA, Dunning TH Jr, Harrison RJ (1992) J Chem Phys 96: 6796
9. Dunning TH Jr (1989) J Chem Phys 90: 1007
10. Peterson KA, Woon DE, Dunning TH Jr (1994) J Chem Phys 100: 7410
11. Wilson A, Mourik van T, Dunning TH Jr (1997) J Mol Struct (THEOCHEM) 388: 339
12. Head-Gordon M, Pople JA, Frisch MJ (1988) Chem Phys Lett 153: 503
13. Frisch MJ, Head-Gordon M, Pople JA (1990) Chem Phys Lett 166: 275
14. Frisch MJ, Head-Gordon M, Pople JA (1990) Chem Phys Lett 166: 281
15. Head-Gordon M, Head-Gordon T (1994) Chem Phys Lett 220: 122
16. Saebo S, Almlof J (1989) Chem Phys Lett 154: 83
17. Krishnan R, Pople JA (1978) Int J Quantum Chem 14: 91
18. Pople JA, Head-Gordon M, Raghavachari K (1987) J Chem Phys 87: 5968
19. Raghavachari K, Trucks GW, Pople JA, Head-Gordon M (1989) 157: 479
20. Frisch MJ, Trucks GW, Schlegel HB, Gill PMW, Johnson BG, Robb MA, Cheeseman JR, Keith T, Petersson GA, Montgomery JA, Raghavachari K, Al-Laham MA, Zakrzewski VG, Ortiz JV, Foresman JB, Cioslowski J, Stefanov BB, Nanayakkara A, Challacombe M, Peng CY, Ayala PY, Chen W, Wong MW, Andres JL, Replogle ES, Gomperts R, Martin RL, Fox DJ, Binkley JS, Defrees DJ, Baker J, Stewart JP, Head-Gordon M, Gonzalez C, Pople JA (1995) Gaussian 94. Gaussian, Pittsburgh, Pa
21. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA, Jr., Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Baboul AG, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Andres JL, Gonzalez C, Head-Gordon M, Replogle ES, Pople JA (1998) Gaussian 98. Gaussian, Pittsburgh, Pa
22. Werner H-J, Knowles PJ, with contributions from Amos RD, Berning A, Cooper DL, Deegan MJO, Dobbyn AJ, Eckert F, Hampel C, Hetzer G, Leininger T, Lindh R, Lloyd AW, Meyer W, Mura ME, Nicklaß A, Palmieri P, Peterson K, Pitzer R, Pulay P, Rauhut G, Schütz M, Stoll H, Stone AJ, Thorsteinsson T (1996) MOLPRO 96 (a package of ab initio programs). University of Birmingham, UK
23. Frisch Æ, Frisch MJ (1999) Gaussian 98 user's reference, 2nd edn. Gaussian, Pittsburgh, Pa
24. Becke AD (1993) J Chem Phys 98: 5648
25. Klopper W (1995) J Chem Phys 102: 6168
26. Xantheas SS (1996) J Chem Phys 104: 8821
27. Weis P, Kemper PR, Bowers MT, Xantheas SS (1999) J Am Chem Soc 121: 3531
28. (a) Schwenke DW, Truhlar DG (1985) J Chem Phys 82: 2418; (b) (1985) J Chem Phys 86: 3760 (E)