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# Accurate ab Initio Binding Energies of Alkaline Earth Metal Clusters

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The effects of basis set superposition error (BSSE) and core-correlation on the electronic binding energies of alkaline earth metal clusters $Y_n$ (Y = Be, Mg, Ca; $n = 2-4$) at the Moller−Plesset second-order perturbation theory (MP2) and the single and double coupled cluster method with perturbative triples correction (CCSD(T)) levels are examined using the correlation consistent basis sets cc-pVXZ and cc-pCVXZ (X = D, T, Q, 5). It is found that, while BSSE has a negligible effect for valence-electron-only-correlated calculations for most basis sets, its magnitude becomes more pronounced for all-electron-correlated calculations, including core electrons. By utilizing the negligible effect of BSSE on the binding energies for valence-electron-only-correlated calculations, in combination with the negligible core-correlation effect at the CCSD(T) level, accurate binding energies of these clusters up to pentamers (octamers in the case of the Be clusters) are estimated via the basis set extrapolation of ab initio CCSD(T) correlation energies of the monomer and cluster with only the cc-pVDZ and cc-pVTZ sets, using the basis set and correlation-dependent extrapolation formula recently devised. A comparison between the CCSD(T) and density functional theory (DFT) binding energies is made to identify the most appropriate DFT method for the study of these clusters.

## I. Introduction

In recent years, studies on the structural and energetic properties of alkaline earth metal clusters have received a lot of attention because of their role as intermediates for the transition from isolated gas-phase molecules to the bulk solid-state phase.[1−10] Starting from weakly bound van der Waals dimers, although the small clusters exhibit properties such as nonmetallic insulator, their properties change to metallic conductor at some point as the size of the clusters increases. The size of the cluster at which this transition occurs appears to vary, depending on the kind of metal clusters, and is currently a subject of intense experimental and theoretical investigations by various workers.[2,5,6]

It is now well recognized that the application of the ab initio wave function theoretical approach to large molecular clusters has two formidable problems to overcome for a successful outcome of the theory: electron correlation treatment and basis set expansion of the wave function. These two problems, which are separate in some sense and interrelated in another sense, are primarily responsible for the limited usage of more systematic wave function approaches in studying the large molecular clusters compared to density functional theory (DFT)-based approaches. However, although DFT-based methods have been effective in elucidating the various isomeric structures and related properties such as vibrational frequencies and polarizabilities of metal clusters,[1,4,7,11−13] an accurate determination of binding energies by DFT methods appears to be a difficult task because the computed binding energies often change significantly with the kind of density functionals chosen for the system.[14,15] This makes basis set extrapolation techniques exploiting the convergent behavior of the correlation consistent basis sets cc-pVXZ (X = D, T, Q, 5, 6)[16−21] attractive, especially if extrapolation is adaptable to ab initio computations with small basis sets. In this sense, among the various extrapolation formulas and methods suggested previously,[22−35] the extrapolation formula recently devised by Huh and Lee,[32] which is based on fitting two successive correlation energies with the correlation consistent basis sets cc-pVXZ and cc-pV(X+1)Z (X = D(2), T(3), Q(4)) by $(X + \alpha)^{-3}$ to estimate the basis set limit correlation energy at the MP2[36] and CCSD(T)[37] levels, appears to be a good choice for application to large molecular clusters ($\alpha$ is a parameter varying with the correlation level and basis set quality employed). The results obtained from extrapolation were quite impressive; for extrapolation with the cc-pVDZ and cc-pVTZ basis sets applied to various relatively small clusters, such as dimers and trimers,[14,32] the estimated complete basis set (CBS) limit binding energies were found to be close to the exact CBS limits within error bounds in many cases, suggesting the aforementioned basis set extrapolation method could be applied to large clusters of more than a few monomers. However, to extend this technique to much larger clusters than those previously examined, two important issues relevant to the wave-function-based correlation approach, such as the MP2 or CCSD(T) method, must be also clarified. First, because the previous extrapolation studies[14,22] were performed on the counterpoise (CP)[38] corrected binding energies using the basis set of the cluster, the effect of basis set superposition error (BSSE)[39] on binding energies in the case of uncorrected computations (using monomer basis sets) must be examined, which could significantly reduce the computational demand. Second, as the usual ab initio computation is performed under frozen-core approximation (FCA; valence-electron-only correlation), the effect of core-correlation, introduced by activating the core orbitals, must also be accounted for to accurately estimate the binding energies in correlated calculations. The purpose of this article is to investigate the effects of these two factors on the binding energies of alkaline earth metal clusters $Y_n$ (Y = Be, Mg, Ca; $n = 2$ up to 8 in the case of Be) and lay a foundation for the general application of the basis set extrapolation technique to larger clusters than those studied here. In addition to that, using the accurate CBS limit CCSD(T) binding energy estimates obtained through our basis set

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**TABLE 1: Basis Set Convergence of Binding Energies (in m$E_h$) under Frozen-Core Approximation**

| | X$^{a}$ | $Be_2$ (5.00)$^{b}$ | $Be_3$ (4.20) | $Be_4$ (3.90) | $Mg_2$ (7.352) | $Mg_3$ (6.373) | $Mg_4$ (5.877) | $Ca_2$ (4.270) | $Ca_3$ (3.933) | $Ca_4$ (3.767) |
|---|---|---|---|---|---|---|---|---|---|---|
| MP2 | D | −0.45(−0.74)$^{c}$ | 36.6(35.2) | 144.2(141.1) | 0.19(0.04) | 5.1(4.3) | 35.5(33.5) | 1.54(1.20) | 13.0(11.9) | 49.0(46.6) |
| | T | 1.34(1.10) | 44.6(43.5) | 162.8(160.5) | 1.17(1.08) | 8.8(8.4) | 43.9(42.9) | 2.84(2.66) | 19.2(18.5) | 62.9(61.6) |
| | Q | 1.75(1.61) | 47.2(46.6) | 168.9(167.7) | 1.51(1.45) | 10.2(9.9) | 47.0(46.4) | 3.45(3.33) | 21.5(21.1) | 67.8(66.9) |
| | 5 | 1.97(1.88) | 48.2(47.9) | 170.8(170.0) | 1.60(1.56) | 10.5(10.9) | 48.3(47.8) | 3.59(3.50) | 22.1(21.8) | 69.1(68.4) |
| | CBS$^{d}$ | 2.18 | 49.6 | 173.0 | 1.8 | 11.4 | 50.0 | 3.66$^{f}$ | 22.5$^{f}$ | 69.9$^{f}$ |
| | D−T$^{e}$ | 2.48(2.25) | 50.2(49.3) | 175.5(173.6) | 1.83(1.78) | 11.4(11.2) | 50.2(49.6) | 3.70(3.63) | 23.2(23.0) | 72.4(71.8) |
| CCSD(T) | D | −0.40(−0.53) | 24.6(24.1) | 107.7(106.5) | −0.10(−0.17) | 3.6(3.3) | 26.5(25.7) | 1.80(1.68) | 12.5(12.1) | 40.1(40.9) |
| | T | 1.70(1.61) | 33.6(33.2) | 129.3(128.5) | 1.17(1.14) | 8.5(8.4) | 37.4(37.1) | 3.65(3.63) | 21.5(21.4) | 60.3(60.1) |
| | Q | 2.20(2.18) | 36.3(36.2) | 135.6(135.4) | 1.58(1.56) | 10.2(10.1) | 40.9(40.7) | 4.47(4.45) | 24.4(24.3) | 65.8(65.7) |
| | 5 | 2.46(2.45) | 37.2(37.2) | 137.3(137.2) | 1.67(1.66) | 10.4(10.9) | 42.0(41.9) | 4.64(4.63) | 24.9(24.9) | 66.9 |
| | CBS$^{f}$ | 2.67 | 37.9 | 138.7 | 1.74 | 10.9 | 43.0 | 4.81 | 26.2 | 67.9 |
| | D−T$^{e}$ | 2.78(2.70) | 38.7(38.3) | 141.4(140.7) | 1.86(1.85) | 11.3(11.3) | 43.9(43.8) | 4.66(4.67) | 26.5(26.5) | 71.1(71.1) |

[a] cc-pVXZ (X = D, T, Q, 5) basis set. [b] Values in parentheses are the bond distances in the cluster (in bohr). Trimers and tetramers are in $D_{3h}$ and $T_d$ symmetry, respectively. [c] Values in parentheses are the CP-corrected binding energies. [d] Reference MP2 CBS limits are from ref 43, except for the Ca clusters. [e] Estimated CBS limit binding energies with cc-pVDZ and cc-pVTZ basis sets in which the correlation contribution to the binding energies were obtained from extrapolation by eq 2 in the text. [f] Reference CBS limits were obtained through the extrapolation of the CP-corrected correlation contribution to the binding energies with cc-pVQZ and cc-pV5Z basis sets by $X^{-3}$ ($X$ = 4, 5).

extrapolation method and some reference CBS limit results, which are expected to be close to the full configuration interaction (FCI) CBS limit or experimental binding energies, we evaluate the performance of various DFT methods and search for the most suitable DFT method which can yield accurate and reliable binding energies for these kinds of clusters.

In the next section, the extrapolation method and computational procedures employed in this study are explained. In section III, the results and discussion are presented. The summary and conclusion are in section IV.

## II. Theoretical Method

To investigate the effect of BSSE and core-correlation on electronic binding energies of alkaline earth metal clusters in correlated calculations, two separate calculations were performed. First, the binding energies of $Y_n$ (Y = Be, Mg, Ca; $n$ = 2, 3, 4) were computed at the MP2 and CCSD(T) level with and without CP correction[38] for BSSE under FCA with the cc-pVXZ (X = D, T, Q, 5) basis sets. Second, the same CP-corrected and uncorrected computations—but with all electrons correlated, including the core—employing the cc-pCVXZ (X = D, T, Q) basis sets,[40−42] which contain core-correlating functions in addition to valence-optimized cc-pVXZ basis sets, were performed. While the smallest cc-pVDZ sets consist of [3s2p1d] for the Be atom, [4s3p1d] for the Mg atoms, and [5s4p2d] for the Ca atoms, the largest cc-pV5Z sets contain [6s5p4d3f2g1h] for the Be atom, [7s6p4d3f2g1h] for the Mg atoms, and [8s7p5d3f2g1h] for the Ca atoms. Then, to estimate the basis set limit correlation energy $E_{\mathrm{CORR}}(\infty)$ (or the correlation contribution to the binding energy, $\Delta E_{\mathrm{CORR}}(\infty)$), the correlation energies $E_{\mathrm{CORR}}(X)$ of the fragments and cluster (or $\Delta E_{\mathrm{CORR}}(X)$) with the cc-pVDZ and cc-pVTZ sets (cc-pCVDZ and cc-pCVTZ in the case of an all-electron correlation calculation) were extrapolated by the following formula recently suggested by Huh and Lee for correlation consistent basis set calculations:[32]

$$E_{\mathrm{CORR}}(X) = E_{\mathrm{CORR}}(\infty) + A(X + \alpha)^{-3},\ \ X = 2, 3 \qquad (1)$$

or

$$\Delta E_{\mathrm{CORR}}(X) = \Delta E_{\mathrm{CORR}}(\infty) + A(X + \alpha)^{-3},\ \ X = 2, 3 \quad (2)$$

in which

$$\Delta E_{\mathrm{CORR}}(X) = nE_{\mathrm{CORR}}(X)[\mathrm{Y}] - E_{\mathrm{CORR}}(X)[\mathrm{Y}_n]$$

Here, α is the correlation-dependent parameter that is introduced to compensate for the incompleteness of the basis sets employed in the extrapolation (1.0 at the MP2 and 0.5 at the CCSD(T) level). Initially, for a comparison of the computed and extrapolated results with the reference CBS limit binding energies, which were taken as the highly accurate MP2−R12 results by Klopper and Almlof in the case of Be and Mg clusters,[43] all ab initio computations for Be and Mg clusters were performed at geometries in which R12 reference results were known. For Ca clusters for which accurate CBS limit binding energies are not available from the literature, the ab initio computation of binding energies was performed at the geometries optimized using the hybrid B3PW91 DFT method,[44,45] except in the case of $Ca_2$, for which the computation was performed at the experimental geometry to compare with the experimental binding energy available. The experimental and B3PW91 optimized equilibrium geometries for $Ca_2$ are almost the same (8.08 vs 8.07 bohr).

After establishing the accuracy of the extrapolated results with respect to the reference CBS limits, the comparison between ab initio extrapolated CBS limit binding energies and the results based on DFT methods was made for dimers up to pentamers (up to octamers in the case of Be clusters) of these clusters at the geometries optimized by DFT methods previously.[1,4,7] The DFT methods examined in this study include the gradient-corrected BP86[46] and BPW91[47] methods, along with hybrid B3LYP[48−50] and B3PW91[44,45] methods. These methods are among the most frequently used DFT methods for these clusters, along with the DFT methods based on local density approximation (LDA). All DFT computations were carried out with 6-311+G(3df) basis set, which appeared to yield binding energies close to the CBS limit DFT results within 0.1−0.2 m$E_h$ for the dimers (1 m$E_h$ = 0.6275 kcal/mol). All computations were carried out by ACES II[51] and Gaussian 98[52] program packages.

## III. Results and Discussion

In Table 1 the basis set convergence of the CP-corrected and uncorrected binding energies toward the corresponding CBS limits of small alkaline earth metal clusters at the MP2 and CCSD(T) levels with valence-electron-only correlation is presented along with the CBS limit estimates obtained through the

**TABLE 2: Basis Set Convergence of Binding Energies (in $mE_h$) with All Electrons Correlated[a]**

| | X[b] | $Be_2$ | $Be_3$ | $Be_4$ | $Mg_2$ | $Mg_3$ | $Mg_4$ | $Ca_2$ | $Ca_3$ | $Ca_4$ |
|---|---|---|---|---|---|---|---|---|---|---|
| MP2 | D | −0.17(−0.59)[c] | 37.9(35.7) | 148.6(143.3) | 0.55(0.12) | 7.1(4.6) | 41.3(35.7) | 2.82(1.65) | 16.2(12.2) | 55.7(47.2) |
| | T | 1.50(1.24) | 45.2(44.2) | 165.6(163.3) | 1.66(1.24) | 10.6(8.8) | 48.0(43.2) | 4.21(3.46) | 24.1(20.8) | 74.7(66.9) |
| | Q | 1.93(1.80) | 48.2(47.6) | 172.2(171.0) | 1.78(1.62) | 11.2(10.4) | 48.7(46.7) | 4.68(4.22) | 26.0(24.0) | |
| | CBS[d] | 2.41 | 50.8 | 176.7 | 1.98 | 12.0 | 50.3 | 4.62 | 25.8 | 75.2[g] |
| | D−T[e] | 2.65(2.39) | 50.0(49.8) | 176.4(176.1) | 2.39(1.99) | 12.9(11.6) | 52.5(49.6) | 5.13(4.66) | 29.4(26.6) | 87.8(80.2) |
| CCSD(T) | D | −0.12(−0.38) | 26.3(25.0) | 113.0(109.7) | 0.21(−0.15) | 5.3(3.2) | 31.7(25.2) | 2.51(1.44) | 14.2(10.7) | 45.6(37.8) |
| | T | 1.85(1.75) | 34.9(34.5) | 133.2(132.3) | 1.50(1.12) | 9.5(7.9) | 40.1(35.8) | 4.01(3.39) | 23.1(20.3) | 66.4(59.5) |
| | Q | 2.38(2.35) | 37.8(37.7) | 139.8(139.5) | 1.60(1.48) | 10.0(9.4) | 40.5 | 4.52(4.15) | 25.1(23.5) | |
| | CBS[f] | 2.86 | 39.5 | 143.0 | 1.62 | 10.1 | 41.7[g] | 4.47 | 25.6 | 67.3[g] |
| | D−T[e] | 2.86(2.83) | 39.5(39.6) | 143.8(144.1) | 2.18(1.78) | 11.8(10.5) | 44.7(41.5) | 4.81(4.42) | 27.9(25.5) | 77.7(71.3) |

[a] Geometries of the clusters are the same as those in Table 1. [b] cc-pCVXZ (X = D, T, Q) basis set. [c] Values in parentheses are the CP-corrected binding energies. [d] Reference CBS limit values are from ref 43 for the Be and Mg clusters. For the Ca clusters, except $Ca_4$, the reference values were obtained by adding the estimated core-correlation corrections at the basis set limit to the valence-only-correlated MP2 CBS limits in Table 1 (see text). [e] Estimated CBS limit binding energies with cc-pCVDZ and cc-pCVTZ basis sets for which the correlation contributions to the binding energies were obtained from extrapolation by eq 2 in the text. [f] The reference values were obtained by adding the estimated core-correlation corrections at the basis set limit to the valence-only-correlated CCSD(T) CBS limits in Table 1, except for $Mg_4$ and $Ca_4$ (see text). [g] The reference values were obtained by adding the core-correlation corrections with TZ basis quality to the valence-only-correlated CBS limits in Table 1 (see text).

extrapolation of the cc-pVDZ and cc-pVTZ basis set results. While the MP2 reference CBS limits for Be and Mg clusters were taken from the highly accurate R12 results in ref 43, the remaining reference CBS limits were obtained through the extrapolation of the CP-corrected correlation contributions to the binding energies with the cc-pVQZ and cc-pV5Z sets by $X^{-3}$ ($X = 4,5$), which were then added to the converged Hartree−Fock (H−F) contributions. While the H−F contributions to the reference and estimated CBS limit binding energies were taken from the near H−F limit results in ref 30 for Be and Mg clusters, the CP-corrected H−F binding energies with the cc-pV5Z basis set were employed for the corresponding H−F contributions for Ca clusters.

First of all, Table 1 shows that one can get a very good estimate to the CBS limit, even with the small basis set results, if one adopts the appropriate extrapolation formula relevant to basis set and correlation level employed. It is worth noting that the DZ-TZ extrapolated estimates in both the CP-corrected and uncorrected calculations are closer to the basis set limits than are the corresponding results with the cc-pV5Z basis set for these clusters in most cases, which signifies the utility of the employed extrapolation formula for large clusters. Second, except for the weakly bound dimers, BSSE has a negligible effect on the binding energies for these clusters, even when relatively small basis sets such as cc-pVDZ and cc-pVTZ are used. It is interesting to note that, even with the use of the smallest cc-pVDZ set, the BSSE is usually within 10% of the total binding energy. This is in contrast to the other weakly bound clusters such as van der Waals and hydrogen-bonded clusters in which BSSE has a significant effect on the binding energy when basis sets are not sufficiently large.[52−57] Another interesting finding is that, although the CP-corrected DZ-TZ extrapolated binding energies are closer to the reference CBS limits than are the uncorrected counterparts in most cases, extrapolation is also beneficial to reduce the effect of BSSE because the difference between the CP-corrected and uncorrected DZ-TZ extrapolated estimates is smaller than the difference between the CP-corrected and uncorrected binding energies with the cc-pVDZ or cc-pVTZ basis set. Therefore, for correlated calculations under FCA, extrapolation of the uncorrected correlation binding energies with the cc-pVDZ and cc-pVTZ basis sets, according to eq 2, appears to provide a reliable and accurate estimate of the basis set limit for these clusters.

In Table 2 we present the corresponding results to Table 1 with all electrons being correlated using the cc-pCVXZ (X = D, T, Q) sets, which contain extra core-correlating functions to the valence-optimized cc-pVXZ sets. The D−T results in this case, therefore, correspond to the estimated basis set limits obtained through the extrapolation of correlation energies with the cc-pCVDZ and cc-pCVTZ sets by eq 1. While the MP2 reference CBS limits for Be and Mg clusters in Table 2 were taken from the highly accurate R12 results in ref 43, the remainder of the reference CBS limits in Table 2 were obtained by adding the reference CBS limits in Table 1 to the core-correlation corrections. The core-correlation corrections at the basis set limit were estimated by the $X^{-3}$ extrapolation of the differences between the CP-corrected cc-pVXZ results in Table 1 and the cc-pCVXZ results in Table 2 (X = T(3), Q(4)), except for $Mg_4$ at the CCSD(T) level and $Ca_4$ at the MP2 and CCSD(T) levels, for which the core-correlation corrections were taken as the differences between the CP-corrected cc-pVTZ results in Table 1 and the cc-pCVTZ results in Table 2.

From the results in Table 2, in conjunction with the corresponding results in Table 1, several important points can be made about the core-correlation effect in the computation of the binding energies of these clusters. First, except for Be clusters in which core-correlation increases the binding energies by similar magnitudes in both the CP-corrected and uncorrected calculations with basis sets larger than the cc-pCVDZ set, the CP correction for BSSE appears to be very important for the correct estimate of the core-correlation effect on the computed binding energies unless the basis set is sufficiently large. This is well manifested in Table 3 in which the core-correlation effect (the difference between the binding energies in Table 1 and Table 2) on the binding energies is shown for the uncorrected and CP-corrected calculations. If one examines the basis set convergence of the core-correlation effect toward the CBS limit, it is interesting to note that, while the core-correlation effect appears to be adequately represented with the cc-pCVDZ or cc-pCVTZ basis set in most of the CP-corrected calculations, basis sets larger than the cc-pCVTZ set often appear necessary in the uncorrected (BSSE contaminated) calculations for the correct manifestation of the core-correlation effect. This is in contrast to the valence-electron-only correlation results in Table 1, in which the uncorrected and CP-corrected binding energies become very similar with basis sets larger than the cc-pVDZ set. For example, in the case of $Mg_4$ and $Ca_4$ clusters, while the differences between the uncorrected and CP-corrected CCSD(T) binding energies with the cc-pVTZ basis sets in Table 1 only amount to 0.3 and 0.2 $mE_h$, respectively, the correspond-

**TABLE 3: Core-Correlation Effect[a] (in m$E_h$) on the Binding Energies at the MP2 and CCSD(T) Levels**

| | X[b] | $Be_2$ | $Be_3$ | $Be_4$ | $Mg_2$ | $Mg_3$ | $Mg_4$ | $Ca_2$ | $Ca_3$ | $Ca_4$ |
|---|---|---|---|---|---|---|---|---|---|---|
| MP2 | D | 0.28(0.15)[c] | 1.1(0.5) | 4.4(2.2) | 0.36(0.08) | 2.0(0.2) | 5.7(0.1) | 1.28(0.45) | 3.2(0.3) | 6.7(0.6) |
| | T | 0.16(0.14) | 0.6(0.7) | 2.8(2.8) | 0.49(0.16) | 1.8(0.4) | 4.0(0.3) | 1.37(0.80) | 4.9(2.3) | 11.8(5.3) |
| | Q | 0.18(0.19) | 1.0(1.0) | 3.3(3.3) | 0.27(0.17) | 1.0(0.5) | 1.7(0.3) | 1.23(0.89) | 4.5(2.9) | |
| | CBS[d] | 0.23 | 1.2 | 3.7 | 0.18 | 0.6 | 0.3 | 0.96 | 3.3 | |
| | D−T[e] | 0.17(0.14) | −0.2(0.5) | 0.9(2.5) | 0.56(0.21) | 1.5(0.4) | 2.3(0.0) | 1.45(1.04) | 6.3(4.3) | 15.6(8.7) |
| CCSD(T) | D | 0.28(0.15) | 1.7(0.9) | 5.3(3.2) | 0.31(0.02) | 1.7(−0.1) | 5.2(−0.5) | 0.71(−0.24) | 1.7(−1.4) | 4.7(−2.3) |
| | T | 0.15(0.14) | 1.3(1.3) | 3.9(3.8) | 0.33(−0.02) | 1.0(−0.5) | 2.7(−1.3) | 0.36(−0.24) | 1.6(−1.1) | 6.1(−0.6) |
| | Q | 0.18(0.17) | 1.5(1.5) | 4.2(4.1) | 0.02(−0.08) | −0.2(−0.7) | −0.4 | 0.05(−0.30) | 0.7(−0.8) | |
| | CBS[d] | 0.19 | 1.6 | 4.3 | −0.12 | −0.8 | | −0.34 | −0.6 | |
| | D−T[e] | 0.08(0.13) | 0.8(1.3) | 2.4(3.4) | 0.32(−0.07) | 0.5(−0.8) | 0.8(−2.3) | 0.2(0.2) | 1.6(0.3) | 6.9(0.4) |

[a] Differences between the binding energies with valence-electron-only correlation (Table 1) and all-electron correlation (Table 2). [b] The cc-pVXZ basis set was used for the valence-electron-only correlation, and the cc-pCVXZ basis set was used for the all-electron correlation calculations (X = D, T, Q). [c] Values in parentheses are for the CP-corrected binding energies. [d] T−Q extrapolated values by $X^{-3}$ (see text). [e] Differences between the DZ-TZ extrapolated results in Table 1 and those in Table 2.

**TABLE 4: Ab Initio[a] and DFT[b] Binding Energies (in m$E_h$) of Alkaline Earth Metal Clusters[c]**

| | $Be_2$ | $Be_3$ | $Be_4$ | $Be_5$ | $Be_6$ | $Be_7$ | $Be_8$ | $Mg_2$ | $Mg_3$ | $Mg_4$ | $Mg_5$ | $Ca_2$ | $Ca_3$ | $Ca_4$ | $Ca_5$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| MP2 | 2.02 | 49.6 | 174.5 | 255.7 | 300.4 | 389.5 | 500.8 | 1.72 | 12.6 | 52.9 | 63.5 | 3.70 | 23.3 | 72.4 | 101.0 |
| CCSD(T) | 3.07 | 38.0 | 140.6 | 198.7 | 243.1 | 320.7 | 403.0 | 1.93 | 12.7 | 46.7 | 55.3 | 4.66 | 26.4 | 71.7 | 96.7 |
| B3LYP | 7.01 | 51.4 | 155.3 | 214.0 | 263.3 | 342.7 | 420.9 | 0.40 | 4.8 | 22.5 | 26.4 | 2.92 | 17.0 | 48.8 | 66.4 |
| B3PW91 | 9.55 | 59.1 | 172.7 | 236.0 | 294.0 | 380.9 | 468.5 | 3.13 | 15.0 | 45.9 | 57.3 | 6.55 | 29.7 | 75.4 | 103.2 |
| BP86 | 13.18 | 66.8 | 181.1 | 249.2 | 302.1 | 392.5 | 484.7 | 3.54 | 15.9 | 46.2 | 58.0 | 7.35 | 33.2 | 80.7 | 112.3 |
| BPW91 | 12.25 | 67.5 | 183.4 | 251.8 | 306.3 | 397.7 | 491.5 | 3.21 | 17.7 | 50.7 | 64.1 | 8.21 | 36.3 | 87.4 | 121.6 |
| experiment | 3.6[d] | | | | | | | 1.6[e] | | | | 4.9[f] | | | |

[a] MP2 and CCSD(T) binding energies are the estimated CBS limits obtained through the extrapolation of the correlation energies of the fragments and complex under FCA with cc-pVDZ and cc-pVTZ basis sets by eq 1 in the text. [b] DFT binding energies were computed with 6-311+G(3df) basis sets. [c] Geometries optimized by the DFT methods. For $Ca_2$, MP2 and CCSD(T) results correspond to the results obtained at the experimental geometry (see text). [d] From ref 63. [e] From ref 64. [f] From ref 65.

ing differences between the uncorrected and CP-corrected binding energies with the cc-pCVTZ basis set in Table 2 amount to 4.3 and 6.9 m$E_h$, respectively. Generally, the core-correlation effect on the binding energies in the uncorrected calculations appears to be larger than the corresponding effect in the CP-corrected calculations for these clusters, albeit there are some exceptions in the case of Be clusters. This overestimation of the core-correlation effect on the binding energies in the uncorrected calculations is also very well manifested in the extrapolated CBS limit binding energy estimates in which the uncorrected DZ-TZ extrapolated results appear to be much larger (and further away from the reference CBS limits in many cases) than the corresponding CP-corrected extrapolated DZ-TZ results in the case of Mg and Ca clusters. Second, the core-correlation effect on the binding energies of Mg and Ca clusters appears to be strongly dependent on the correlation treatment employed, generally exhibiting a much smaller effect on the binding energy at the CCSD(T) level compared to that at the MP2 level. Considering that the CCSD(T) binding energies would be closer to the FCI results or experimental results than would the MP2 binding energies, the minor effect on the binding energy by core-correlation at the CCSD(T) level would imply that one can accurately estimate the CBS limit binding energies by the extrapolation of the uncorrected correlation binding energies with only valence electrons being correlated. This is well manifested by the generally good agreement between the DZ-TZ extrapolated results of the uncorrected binding energies under FCA in Table 1 and the reference basis set limit binding energies with all electrons correlated in Table 2. Therefore, it could be concluded that, except for the weakly bound dimers, inclusion of core orbitals in the correlation treatment does not appear to have a significant bearing on the total magnitude of the binding energies for these clusters at a highly correlated level such as CCSD(T). Our results also suggest that, when one is interested in the precise effect of core-correlation, CP correction for the BSSE must be performed in the computation, and these CP-corrected binding energies must also be employed in the basis set extrapolation unless the basis set is sufficiently large.

Since it has been shown from previous discussion that the cc-pVDZ and cc-pVTZ basis set extrapolation of CCSD(T) correlation (or correlation binding) energies without CP correction under FCA could yield accurate estimates to the CBS limits for these clusters, we now compare ab initio (MP2 and CCSD(T)) and DFT binding energies for alkaline earth metal clusters $Y_n$ (Y = Be, Mg, Ca), up to $n = 8$ in the case of Be clusters, to evaluate the accuracy of various DFT methods in Table 4. All binding energies in Table 4 were obtained at the equilibrium geometries of the clusters optimized by DFT methods previously.[1,4,7] The MP2 and CCSD(T) binding energies in Table 4 are composed of correlation contributions obtained by DZ-TZ extrapolation of the correlation energies by eq 1 and the H−F contribution obtained by extrapolation of the H−F energies with the cc-pVDZ and cc-pVTZ basis sets using $X^{-3.4}$ ($X = 2,3$).[27] The latter extrapolation formula was adopted as it was found to yield the accurate estimates to the H−F limit binding energies for the clusters of small size ($n < 5$).

With respect to the CCSD(T) binding energies, which should be considered the closest results to the actual binding energies among the reported values in Table 4, the MP2 and DFT binding energies exhibit interesting patterns depending upon the method employed. While the MP2 binding energies appear to be consistently larger than the corresponding CCSD(T) binding energies (although the MP2 binding energies of Mg and Ca dimers and trimers appear to be smaller than the corresponding CCSD(T) values in Table 4, corrections for the core-correlation effect in Table 3 would make the MP2 binding energies larger than the CCSD(T) results), DFT results exhibit a strong dependence on the functionals employed. Starting from the

B3LYP method, which gives the smallest binding energies among all DFT methods employed, the binding energies tend to increase as the method (functional) changes to B3PW91 to BP86 and BPW91. In view of the difference between the B3LYP and B3PW91 results, it is apparent that employment of the Lee−Yang−Parr (LYP) functional[49] is responsible for decreased binding energies in these clusters compared to the other DFT results. This is supported by the previous results for Be and Mg clusters, which found similar decreased binding energies when the B1LYP functional was employed.[14] By contrast, the B3PW91, BP86, and BPW91 methods tend to overestimate the binding energies of these clusters, as was the case for the DFT method based on the LDA.[58−60] The much better agreement of the hybrid B3PW91 results with the CCSD(T) results compared to the corresponding agreement of the gradient-corrected BPW91 results also suggests the importance of the H−F exchange-type contribution for a reliable estimate of the binding energies in these kinds of clusters. Except for the Be clusters in which the B3LYP method provides the closest results to the CCSD(T) results, the B3PW91 method appears to provide the most reliable and accurate binding energies for these kinds of clusters. While the CCSD(T) and B3PW91 methods yield almost equivalent results for Mg clusters, which agree each other within 2 $mE_h$ in the worst case, the discrepancy between the CCSD(T) and B3PW91 results for Ca clusters tends to slowly increase with the size of cluster. Therefore, it could be concluded that B3PW91 method yields an upper bound to the exact binding energies for Mg and Ca clusters, which may be close within a few $mE_h$ for small clusters consisted of less than 10 atoms. It is rather surprising to observe that except for Be clusters, the hybrid B3LYP method performs poorly for these kinds of clusters because this DFT method has often been found to provide the reasonably accurate estimates to the binding energies of other clusters such as hydrogen-bonded systems.[61,62] This again well demonstrates the limitation of the DFT-based approach compared to a purely ab initio approach such as the CCSD(T) method, which was found to yield reliable results consistently for a wide variety of systems, including weakly bound clusters.

## IV. Summary and Conclusion

In this paper, we have explored the utility of basis set extrapolation in predicting accurate binding energies of alkaline earth metal clusters $Y_n$ (Y = Be, Mg, Ca; $n = 2-8$) by examining the effect of BSSE and core-correlation on ab initio binding energies at the MP2 and CCSD(T) levels. Although BSSE will decrease and become negligible as the basis set becomes larger, some important aspects of BSSE have been observed in relation to core-correlation effect and basis set extrapolation when relatively small basis sets, such as cc-pVDZ and cc-pVTZ, are the only options to be employed for ab initio computation. We also examined the accuracy of the various DFT binding energies by comparing them with highly accurate CCSD(T) binding energies. The conclusion can be summarized as follows.

(1) For valence-electrons-only-correlated calculations, the CP-corrected and uncorrected binding energies at the correlated level appear to be similar to each other, with basis sets containing polarization functions (d and f functions) for these clusters except for the weakly bound dimers. The BSSE is much smaller at the CCSD(T) level than it is at the MP2 level. For example, for the CCSD(T) binding energies of dimers through tetramers with the cc-pVTZ basis sets, the BSSE does not exceed 1 $mE_h$ at most. As a result, the estimated CCSD(T) CBS limit binding energies obtained by extrapolation of the CP-corrected and uncorrected correlation energies with the cc-pVDZ and cc-pVTZ basis sets using the $(X + 1/2)^{-3}$ formula are almost same, differing from each other by less than 1 $mE_h$ in the worst case.

(2) For all-electron correlation calculations, the BSSE is much larger compared to valence-electron-only correlation calculations, nonnegligible even with the cc-pCVTZ basis sets in the case of Mg and Ca clusters. Therefore, CP correction is necessary to correctly evaluate the binding energies of these clusters for all-electron correlation calculations if the basis set is not sufficiently large.

(3) The core-correlation effect on binding energy, which is the difference between the valence-electron-only and the all-electron-correlated binding energies at the basis set limit, depends on the electron correlation level employed. For CP-corrected calculations, the core-correlation effect at the CCSD(T) level appears to be negligible, except for Be clusters.

(4) Consideration of all the factors mentioned above leads to the conclusion that extrapolation of uncorrected (BSSE contaminated) CCSD(T) correlation energies with the cc-pVDZ and cc-pVTZ basis sets under FCA by the $E_{\mathrm{CORR}}(X) = E_{\mathrm{CORR}}(\infty) + A(X + 1/2)^{-3}$ $(X = 2, 3)$ formula yields very good approximate results for the exact CCSD(T) CBS limit binding energies of these clusters. Therefore, it appears computationally feasible to obtain accurate binding energies for larger metal clusters than examined here without resorting to DFT-based or semiempirical methods.

(5) Among various DFT methods, the hybrid B3PW91 method appears to provide the most reliable and accurate binding energies for these clusters, except for the Be clusters, for which the B3LYP method appears to be most appropriate to describe the binding. The different characteristics and properties of the Be clusters compared to those of the Mg and Ca clusters, which must originate from the characteristic $1s^22s^2$ ground electronic configuration of the Be atom, would be related to the difference in the most effective DFT method for these clusters.

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