Final Author Version Feb. 20, 2005
Revised for *J. Phys.Chem. A*

Comparative DFT Study of van der Waals Complexes: Rare-Gas Dimers, Alkaline-Earth Dimers, Zinc Dimer, and Zinc-Rare-Gas Dimers

Yan Zhao and Donald G. Truhlar
Department of Chemistry and Supercomputing Institute, University of Minnesota, Minneapolis, MN 55455-0431

Abstract.

Recent interest in the application of density functional theory prompted us to test various functionals for the van der Waals interactions in the rare gas dimers, the alkaline-earth metal dimers, zinc dimer, and zinc-rare-gas dimers. In the present study, we report such tests for 18 DFT functionals, including both some very recent functionals and some well established older ones. We draw the following conclusions based on the mean errors in binding energies and complex geometries: (1) B97-1 gives the best performance for predicting the geometry of rare-gas dimers, whereas M05-2X and B97-1 give the best energetics for rare gas dimers. (2) PWB6K gives the best performance for the prediction of the geometry of the alkaline-earth metal dimers, zinc dimers, and zinc-rare-gas dimers. M05-2X gives the best energetics for the metal dimers, whereas B97-1 gives the best energetics for the zinc-rare-gas dimers. (3) The M05 functional is unique in providing good accuracy for both covalent transition metal dimers and van der Waals metal dimers. (4)The combined mean percentage unsigned error in geometries and energetics shows that M05-2X and MPWB1K are the overall best methods for the prediction of van der Waals interactions in metal and rare-gas van der Waals dimers.

1. Introduction

The van der Waals interaction is very important for many areas of chemistry such as molecular scattering, chemical-reaction precursor complexes, energy transfer intermediates, molecular recognition, protein folding, stacking of nucleobases, some types of self-assembly and supramolecular chemistry, solvation, condensation, and crystal packing. At long range, van der Waals interactions are dominated by dispersion, induction, and the interaction of permanent multipole moments, and at shorter range they also include contributions from overlap and exchange. Rare gas dimers[1-23] from group 18 of the periodic table are the simplest examples of van der Waals complexes, because they have closed-shell electronic structures and they do not involve permanent multipole moments. Group-2 and group-12 metals (e.g., Be, Mg, Ca, and Zn) have only closed subshells and have no nonzero permanent multipole moments, and thus their complexes also provide especially simple cases of weak interactions. Since density functional theory (DFT) has become the preferred method for first-principles modeling of complex systems, it is of great interest to understand its strengths and limitations for modeling van der Waals complexes, and in this paper we explore the adequacy of a wide variety of functionals for 18-18, 2-2, 12-12, and 12-18 van der Waals dimers (where X-Y denotes a dimer with one atom from group X and the other from group Y). We consider only density functionals that do not add an explicit dipole-dipole term, but rather that model weak interactions in terms of Kohn-Sham Coulomb potentials, local spin densities, density gradients, kinetic energy densities, and Hartree-Fock exchange or in terms of Kohn-Sham Coulomb potentials and local spin densities along with some subset of the three other kinds of functionality.

There have been several previous tests[4,6,7,13,21,23-25] of density functionals for dispersion interactions in rare gas dimers. Patton and Pederson[6] found that some generalized gradient approximation (GGAs), such as PW91[26] and PBE,[27] which involve only Kohn-Sham Coulomb potentials, local spin densities, and density gradients, can give

realistic van der Waals wells for these 18-18 dimers, and they concluded that the interaction resulting from the overlap of atomic densities is the primary binding mechanism in these rare-gas dimers at short range. Zhang et al.[7] tested the local spin density approximation[28] (LSDA) and several[26,27,29] GGA functionals for the same kind of systems. They concluded that the behavior of an exchange functional in the region of small density and large density gradient plays a very important role in the ability of the functionals to describe 18-18 van der Waals attraction; Adamo and Barone[30] and a paper[24] of our own drew similar conclusions. Tao and Perdew[21] noted that a van der Waals complex is bound by the short-range part of the van der Waals interaction and that this is amenable to description by a GGA or a GGA augmented by kinetic energy density, which is called a meta GGA. They tested several functionals (LSDA,[28] PW91,[26] PBE,[27] PBE0[31] (which is also called PBE1PBE and PBEh), and TPSSh[32]), and their results show that the tested functionals tend to overestimate the dispersion interaction energies when the outermost subshell consists of *s* electrons (as in He_2) and underestimate the interaction strength when the valence electrons are *p* electrons, as in Ne_2, Ar_2, and Kr_2. This is confirmed by a recent study of Be_2 by Ruzsinszky et al.[23] and by a study of Ca_2 and Zn_2 by Furche and Perdew.[33]

The van der Waals interactions in the alkaline-earth dimers[34-42] and in the zinc dimer[43-47] are interesting because the outermost subshells are *s* electrons, but alkaline-earth metals and zinc differ from the rare-gas atoms in having much lower ionization potentials and in having nearly degenerate *s*-*p* subshells, as a result of which, their van der Waals wells are much deeper than those of the rare gas dimers. The near degeneracy of *s*-*p* subshells also causes so called multireference effects. For example, Be_2 is a well-known multireference system,[48-51] and the current "gold standard" method for thermochemistry, CCSD(T),[52] seriously underestimates the binding energy of Be_2.[50] The van der Waals interactions in these metal dimers present a stringent test of density functional methods. Ruzsinszky et al.[23] have shown that LSDA, GGA, and meta-GGA

functionals without explicitly empirical parameters overestimate the interaction energy in Be_2.

In the present paper, we provide a broader assessment of DFT for weak interactions by applying a total of 18 functionals to twenty 18-18, 2-2, 12-12, and 12-18 dimers. The functionals tested include all those mentioned above plus other popular functionals, some functionals[24,53-55] that were found to be particularly accurate for weak interactions in previous systematic studies,[24,53] and the newly developed DFT methods M05[56] and M05-2X.[57] The dimers studied include the rare gas dimers, the alkaline-earth dimers (Be_2, Mg_2, and Ca_2), the zinc dimer (Zn_2), and zinc-rare-gas dimers[46,58-60] (ZnNe, ZnAr, and ZnKr). The 2-2, 12-12, and 12-18 systems provide particularly interesting tests of functionals with empirical parameters because systems like this have not been examined during the development of these functionals and the determination of their parameters.

We note that Becke and Johnson recently showed[61-64] that the position-dependent dipole moment of the exchange hole can be used to generate dispersion interactions and accurate C_6, C_8, and C_{10} coefficients, and intermolecular potential-energy surfaces can be obtained from Hartree-Fock occupied orbitals and polarizability data. The present work, however, is limited to models that do not incorporate an explicit dipole-dipole term.

Section 2 describes the calculations. Section 3 presents results and discussion, and Section 4 has concluding remarks.

2. Computational Methods

All calculations are performed self-consistently using a locally modified version of the *Gaussian03* program. We tested the six recently developed semiempirical functionals, MPWB1K,[24] MPW1B95,[24] PW6B95,[53] PWB6K,[53] M05[56] and M05-2X,[57] each of which is a hybrid meta GGA (where "hybrid" denotes the inclusion of Hartree-Fock exchange), because they all showed good performance on noncovalent interactions in our previous studies.[24,53,56,57,65-67] The most recent of these functionals, M05-2X ("Minnesota 2005

functional with double Hartree-Fock exchange") is particular interesting because it has been shown[57] to have good performance for thermochemical kinetics, noncovalent interactions (especially weak interaction, hydrogen bonding, π···π stacking and interactions energies of nucleobases), and alkyl bond dissociation energies. The M05-2X functional results from a new kinetic-energy-density-dependent form for exchange combined in a consistent way with a kinetic-energy-dependent, self-correlation-free correlation functional in a way that allow for using a high fraction of Hartree-Fock exchange without deteriorating performance for main-group thermochemistry. We also tested two hybrid GGAs, in particular B97-1[54] and B98,[55] that were shown in previous studies[24,53] to have especially good performance on the van der Waals interactions of rare-gas dimers. Johnson and DiLabio[68] also recently showed that B97-1 gives good performance for noncovalent interactions; in particular they emphasized the good performance of B97-1 without counterpoise (CP) corrections for the geometry of van der Waals complexes and the good performance of B97-1 with counterpoise corrections for the energies of van der Waals complexes. The present study also tested three functionals, LSDA (SPW91),[28,69] PBE,[70] and TPSS,[71] that have no explicitly empirical parameters, and two of their associated hybrids, namely PBE0[31] and TPSSh[32], each of which has one explicitly empirical parameter, because these have been tested for rare-gas dimers by Tao and Perdew,[21] and PBE0 was found[72] to be the best functional for clusters of Al atoms (note that Al_2 is a 13-13 dimer with a covalent bond rather than a van der Waals bond, and so it is not included in the present paper). We also tested two of the three functionals that were used by Zhang et al.[7] (PW91 and PBEPW91; we exclude the older Becke86A method). We also tested a recent functional[73] specifically developed for water clusters, namely PBE1W. Finally we added two popular hybrid GGA functionals, namely mPW1PW91[30] (also called mPW0 and MPW25) and MPW1K.[74] Note that we did not include the functionals based on the Becke88[75] exchange and LYP[76] correlation (e.g., B3LYP,[77] BLYP, and B1LYP[78]), because they do not predict the existence of van der

Waals wells for most of the rare-gas dimers in the present study, and so they are clearly inappropriate for studying weak interactions.

We first tested these functionals for the ten rare-gas dimers: He_2, Ne_2, Ar_2, Kr_2, HeNe, HeAr, HeKr, NeAr, NeKr, and ArKr. The reference energetic and geometric data for these dimers are taken from the papers by Ogilvie and Wang.[2,3] We also tested these functionals for four metal dimers that are bonded by van der Waals forces: Be_2,[50,51] Mg_2,[34,38,40] Ca_2,[35,38,41] and Zn_2,[44,47] and for three Zn-rare gas dimers: ZnNe,[79] ZnAr,[60] and ZnKr.[80] We do not include the ZnHe dimer, because there are no accurate experimental or theoretical reference data for this dimer.

We used the aug-cc-pVTZ basis set for all rare-gas atoms and for the beryllium and magnesium atoms. *Gausian03*[81] does not include the aug-cc-pVTZ basis set for helium atom, so we obtained the aug-cc-pVTZ basis set for helium from the Extensible Computational Chemistry Environment Basis Set Database.[82] The basis set for calcium is based on the CV(T+2d)Z basis recommended by Iron et al.[42] We augmented this basis by one *s*, one *p*, one *d*, and one *f* diffuse functions on Ca by dividing the most diffuse exponents in the CV(T+2d)Z basis by three; we call this basis aug-CV(T+2d)Z. We used the aug-cc-pVTZ basis for zinc developed by Balabanov and Peterson.[83] The basis sets that are not defined in *Gaussian03* (for He, Ca, and Zn) are presented in Supporting Information. Note that all basis sets in the present study use spherical harmonic sets of *d* and *f* basis functions.

We used the ultrafine integration grid[81] for all calculations in the present study. Although the basis sets are complete enough that counterpoise CP[84,85] corrections for basis set superposition error (BSSE) are small (in general, as shown in our previous work,[25] CP corrections are smaller for DFT than for correlated wave function theories), we performed calculations both with and without CP.

3. Results and Discussion

In this section, we gauge the quality of the results by mean unsigned error (MUE) and mean signed error (MSE). We also discuss the mean percentage unsigned error (M%UE) in section 3.6. In each table, the functionals will be listed in order of the mean errors given in the last column of that table, and the five values of every mean error column that have the smallest absolute values are in bold font. Throughout the paper, mean errors were computed from the original unrounded data, and thus they may differ in the last digit from values computed from the tables in the article. We found that CP corrections have small (although not entirely negligible) effects on the bond lengths of the dimers in the present study, and we give the results for bond lengths with CP only in Supporting Information. However, in the whole article binding energies calculated with CP corrections are calculated at geometries optimized with CP corrections, and binding energies calculated without CP corrections are calculated at geometries optimized without CP corrections.

3.1. Bond lengths for rare gas dimers

The optimized bond lengths of the ten rare-gas dimers are listed in Table 1 and Table S1. (Tables beginning with "S" are in Supporting Information.) Table 1 gives the results without counterpoise corrections, and it shows that two GGAs, namely PBEPW91 and PBE, and three hybrid GGAs, namely, B97-1, B98, and PBE0, give the best performance for calculating the bond length of these rare gas dimers, followed by two hybrid meta GGAs, namely PW6B95 and M05-2X. When the counterpoise correction is turned on (Table S1), the best performers for bond length calculations are B97-1 M05-2X, PBEPW91, B98, and PBE, followed by PW6B95 and the PW91 GGA. Both tables show that the LSDA functional seriously underestimate the bond lengths, whereas the TPSS, TPSSh, mPWPW91, and MPW1K functionals greatly overestimate them.

3.2. Binding energies for rare gas dimers

The calculated binding energies of the ten rare gas dimers are listed in Table 2 and Table 3. Table 2 gives the results without counterpoise corrections, and it shows that M05-2X, B97-1, B98, PBE, and PBEPW91 give the best performance for calculating binding energies, and these methods are also the best five performers with the counterpoise corrections included, as shown in Table 4. In both tables, these five methods are followed by the M05 hybrid meta GGA and by the PBE1W GGA. Table 2 and Table 3 show that PW91 and LSDA overbind these rare gas dimers by a large margin. This is consistent with the assessment of Tsuzuki and Luthi;[86] they also demonstrated that PW91 overbinds some rare-gas dimers. Most of the other functionals underestimate the binding energies; when CP corrections are included, only the PWB6K hybrid meta GGA gives a small positive MSE. Table 2 and Table 3 also show that most of the tested DFT methods overestimate the binding energy of the helium dimer, which is usually considered as an 18-18 van der Waals dimer, despite the absence of *p* electrons. The exception to this overestimation trend is the M05-2X functional with CP corrections; either with or without CP corrections, this functional gives the best agreement with experiment for the helium dimer.

The performance of the PBE and TPSS functionals for He_2, Ne_2, and Ar_2 has also been studied recently by Ruzsinszky et al.,[23] who noted that these functionals do not properly predict the experimentally observed increasing trend in dimer binding energies from He (0.022 kcal/mol) to Ne (0.84 kcal/mol) to Ar (0.285 kcal/mol). Our Table 2 confirms this failure for TPSS and the serious underestimation of the Ne_2/Ar_2 difference by PBE. In fact many of the DFT methods are qualitatively insensitive to the increase in atomic number for these homonuclear dimers and consequently they exhibit a compression in the range of predicted binding energies. The experimental difference in binding energies of Ar_2 and He_2 is 0.26 kcal/mol, and most of the functionals underestimate this by more than a factor of three, giving values of 0.07 kcal/mol or less.

The exceptions and their Ar_2-He_2 difference in kcal/mol are: M05-2X, 0.22; M05, 0.15; PWB6K, 0.12; and B97-1, 0.11. Including CP corrections makes these values slightly worse. It is encouraging that the two functionals with the most recently developed functional form show the best performance, even though this energy difference was not used in their development.

3.3. Bond lengths for metal dimers and zinc-rare-gas dimers

The optimized bond lengths of the four metal dimers and three zinc-rare-gas dimers are listed in Tables 4 and S2. Table 5 gives the results without counterpoise corrections, and it shows that PWB6K, M05-2X, B98, PW6B95, and B97-1 give the best performance for calculating the bond length of these dimers. Table S2 shows that, with the counterpoise correction, the same five functionals are still the best performers for bond length calculations. In both tables these five are followed by the MPWB1K hybrid meta GGA and PBE0, and the eighth through thirteenth positions are also independent of whether or not CP is included. Both tables show that the LSDA functional seriously underestimate the bond lengths.

3.4. Binding energies for metal dimers

The calculated binding energies of the 2-2 and 12-12 metal dimers are listed in Tables 5 and 6. Table 5 gives the results for these van der Waals dimer without counterpoise corrections, and it shows that the functionals with a high percentage of Hartree-Fock exchange, e. g., M05-2X, PWB6K, and MPWB1K, give the best performance for the binding energies of these metal dimers, followed by the PW6B95 and MPW1B95 hybrid meta GGAs. These methods are also the best five performers when the counterpoise corrections are included, as shown in Table 6. Tables 5 and 6 show that the non-hybrid GGA and LSDA functionals seriously overbind these metal dimers. The non-hybrid meta-GGA functionals also perform poorly.

In Tables 5 and 6, we also tabulate a quantity, namely X, which is the percentage of Hartree-Fock exchange in each functional. Tables 5 and 6 show that the performance of

the various functionals for metal dimer van der Waals binding energies correlates with the percentage of Hartree-Fock exchange in the functionals. The general trend is that the higher the percentage of Hartree-Fock exchange, the better the performance of the functionals, probably because Hartree-Fock exchange is self-exchange free, whereas the LSDA, GGA, and meta-GGA exchange functionals have a spurious self-exchange error.[87,88] This self-exchange effect is also associated with the underestimation of the bond lengths for these van der Waals dimers as shown in Tables 4 and S2. These results are very interesting because of the important role of near-degeneracy correlation (also called static correlation, nondynamical correlation, and internal/semi-internal correlation) in metal dimers such as Be_2 and Mg_2. In a recent study[89] of covalently bonded metal dimers, it was found that adding Hartree-Fock exchange made the performance worse, which was interpreted in terms of the importance of static correlation in the GGA exchange functionals[89-91] and the loss of this static correlation when the GGA exchange functional is replaced in part by Hartree-Fock exchange. In later work,[56] it was shown that the M05 functional overcame this problem and gives good results for covalently bonded metal dimers even with $X = 28$. In the metal dimers studied here, though, we obtain good results with many functionals when Hartree-Fock exchange is included. It is interesting that the M05 functional is unique in providing reasonably good performance for both kinds of metal dimers.

3.5. Binding energies for zinc-rare-gas dimers

The calculated binding energies of the three zinc-rare-gas dimers are listed in Tables 7 and 8. Table 7 gives the results without counterpoise corrections, and it shows that B97-1, M05-2X, PWB6K, PBEPW91, and B98 perform best for calculating binding energies of these 12-18 van der Waals dimers. These methods are also the best five performers when counterpoise corrections are included, as shown in Table 8. M05 and PBE are sixth and seventh best, and the eighth through tenth best performers are also

independent of whether or not CP corrections are included. Tables 7 and 8 show that LSDA strongly overbinds these zinc-rare-gas dimers.

3.6. Mean percentage errors

The conclusions in the previous sections are based on the MSE and MUE, neither of which is unitless. To combine the energetic and geometric results, Table 9 provides the mean percentage unsigned error (M%UE). We define three more quantities in Table 9, namely MM%UE, MMM%UE, and MMMM%UE:

MM%UE = 1/2 [M%UE(CP) + M%UE(no-CP)]

MMM%UE = 1/3 [MM%UE(Rg-Rg) + MM%UE (M-M) + MM%UE(Zn-Rg)]

MMMM%UE = 1/2 [MMM%UE(energetics) +MM%UE (geometry)]

where Rg denotes rare gas, and M denotes metal.

The MMMM%UE in Table 9 is our final composite result based on 34 geometry optimizations and 34 energetic calculations at these geometries, and it shows that M05-2X, MPWB1K, B98, MPW1B95, and B97-1 functionals give the lowest overall percentage errors. The M05-2X functional shows amazingly consistent behavior for the mean percentage unsigned error in Table 9; it has the smallest error in 13 of the 14 columns of Table 9, and it trails B98 by only a small margin for the remaining column. This performance is particularly impressive when we recall that the methods in Table 9 were selected (see Section 2) to include methods that were found in previous work to be particularly appropriate for the study of van der Waals interactions, and thus the methods that perform best in Table 9 are “best of the best”. Functionals that appear among the top five in six or more of the 14 columns of Table 9 are M05-2X (all 14), B98 (11), MPWB1K (7), B97-1 (7), PBE0 (7), PW6B95 (6), TPSSh (6), and PWB6K (6).

3.7. Potential energy curves for Be_2 and Ar_2

The potential energy curves for Be_2 and Ar_2 as calculated by the M05-2X, M05, B97-1, TPSS, PBE, and B3LYP density functionals and the Hartree-Fock (HF) method are shown in Figures 1 and 2. For the Be_2 dimer, the Hartree-Fock calculation does not

predict a well, whereas B97-1, TPSS, and PBE significantly overestimate the well depth; M05 and B3LYP are more accurate, and M05-2X gives best agreement with the reference data.

For the Ar_2 dimer, the Hartree-Fock and B3LYP methods do not predict the existence of the van der Waals well, and TPSS and PBE most seriously (of the methods shown) underestimate the well depth; B97-1 and M05 are more accurate, and again the M05-2X functional gives the best agreement with experiment.

4. Concluding Remarks

In the present study, we tested 18 density functionals for the van der Waals interactions in the rare gas dimers, alkaline-earth metal dimers, zinc dimers, and zinc-rare-gas dimers. We draw the following conclusions based on the mean errors in geometries and energetics.

(1) B97-1 gives the best predictions of the geometries of rare gas dimers, whereas M05-2X and B97-1 give the best energetics for rare gas dimers.

(2) PWB6K gives the best predictions of geometries of the alkaline-earth metal dimers, zinc dimers, and zinc-rare-gas dimers. M05-2X gives the best energetics for the metal dimers, whereas B97-1 gives the best energetics for the zinc-rare-gas dimers.

(3) The M05 functional is unique in providing good accuracy for both covalent and noncovalent metal dimers.

(4) The mean percentage unsigned error shows that M05-2X and MPWB1K are the overall best methods for the prediction of geometries and energies of van der Waals interactions in metal and metal-rare gas dimers.

Fourteen of the 18 functionals have final composite percentage errors less than 50% for the 17 weakly bound van der Waals complexes included in this study, and twelve of these functionals have MMM%UE less than or equal to 45%. This latter group of 12 includes all five functionals mentioned already in this section along with seven

others. Several of these functionals are also accurate for main-group atomization energies,[53-57,92,93] heats of formation,[94] bond energies,[57,95] thermochemical kinetics,[53,56,57,96-98] hydrogen bonding,[24,25,53,56,57,65-67,99,100] π···π stacking,[25,53,56,57,65,66] transition-metal dimers,[56,57,89,91] and/or metal-ligand bond energies,[56,57,91,97] but in this respect there are some important distinctions to be made. We will therefore conclude with a brief comparison of these twelve functionals for other properties.

Table 10 compares the top twelve functionals of Table 9 for their performance on several energetic databases. The functionals are listed in the same order as in Table 9. The databases are

- WI17: the 17 weak-interaction complexes in the present article
- NCBE31: the set of 31 nonbonded binding energies including hydrogen bonding, charge transfer complexes, dipole interactions, weak interactions, and π···π stacking.[53] The error shown is the mean mean mean unsigned error.[53]
- TMAE4/05: the set of 4 binding energies of transition-metal dimers.[89 57] The error shown is the average mean unsigned error.[89 57]
- MLAE4/05: the set of 4 binding energies of transition-metal-ligand compounds.[57,91] The error shown is the average mean unsigned error.[57,91]
- MGT135: the set of 135 main group thermochemistry data based on bond energies, ionization potentials, and electron affinities.[101] The error shown is the total mean unsigned error for the MG3S basis set with QCISD/MG3 geometries.[24,53]
- HTK57: the set of 57 hydrogen transfer kinetics data consisting of 38 barrier heights and 19 energies of reaction.[102] The error shown is the average mean unsigned error.

- NHTBH38: the set of 38 non-hydrogen-transfer barrier heights for heavy atom transfer, nucleophilic substitution, association, and unimolecular reaction.[96] The error shown is the mean unsigned error.[96]

The final two columns of Table 10 are the average of the MUEs excluding metals (AMUXM) and the average MUE without exclusions (AMUE). The AMUEXM column shows that, among the twelve functionals that give good results for noncovalent interactions, if we exclude transition-metal compounds, M05-2X is the best general-purpose functional, followed by MPWB1K, PWB6K, and M05. If, however, we include binding energies of transition-metal compounds, the best general functional is M05, followed by TPSSh, B97-1, and B98, as shown by the AMUE column of Table 10.

Acknowledgment. This work was supported in part by the National Science Foundation under Grant No. CHE03-49122 and in part by the Office of Naval Research under grant no. N00012-05-01-0538.

Supporting Information Available: Bond lengths calculated with counterpoise correction are given in the supporting information. The basis sets employed for helium, zinc, and calcium are also given in the supporting information. This material is available free of charge via the Internet at http://pubs.acs.org.

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Table 1: Bond lengths (in Å) of rare-gas dimers without counterpoise correction for BSSE. [a]

Method	He_2	Ne_2	Ar_2	Kr_2	HeNe	HeAr	HeKr	NeAr	NeKr	ArKr	MSE	MUE
Reference	2.97 [b]	3.09 [b]	3.76 [b]	4.01 [b]	3.03 [c]	3.48 [c]	3.69 [c]	3.49 [c]	3.62 [c]	3.88 [c]		
B97-1	2.70	3.02	3.88	4.21	2.85	3.35	3.53	3.46	3.64	4.05	**-0.03**	**0.14**
PBEPW91	2.74	3.09	3.98	4.30	2.92	3.43	3.59	3.54	3.69	4.14	**0.04**	**0.14**
B98	2.78	3.13	4.01	4.34	2.97	3.47	3.63	3.57	3.75	4.17	0.08	**0.14**
PBE	2.75	3.11	4.00	4.33	2.94	3.44	3.60	3.55	3.71	4.17	**0.06**	**0.15**
PBE0	2.80	3.14	4.04	4.37	2.98	3.48	3.72	3.59	3.75	4.20	0.11	**0.15**
PW6B95	3.04	3.22	3.72	4.27	3.00	3.39	3.83	3.57	4.08	4.15	0.13	0.16
M05-2X	2.73	2.87	3.81	4.12	2.79	3.29	3.45	3.34	3.52	3.97	-0.11	0.16
PBE1W	2.75	3.11	4.05	4.39	2.94	3.45	3.61	3.57	3.73	4.22	0.08	0.17
PW91	2.65	3.02	3.95	4.30	2.82	3.34	3.53	3.48	3.64	4.13	**-0.02**	0.17
PWB6K	2.77	2.94	3.71	4.26	2.98	3.38	3.81	3.56	4.07	4.14	**0.06**	0.17
MPW1B95	3.05	3.23	3.73	4.28	3.01	3.40	4.18	3.60	4.09	4.16	0.17	0.20
MPWB1K	3.05	3.23	3.72	4.28	3.01	3.40	4.19	3.60	4.10	4.16	0.17	0.20
M05	2.62	2.86	3.73	4.19	2.74	3.26	3.46	3.31	3.45	3.97	-0.14	0.20
TPSS	2.95	3.23	4.37	4.66	3.04	3.69	3.85	3.74	4.01	4.51	0.30	0.31
TPSSh	2.96	3.23	4.37	4.65	3.04	3.71	3.86	3.82	4.01	4.51	0.31	0.32
LSDA	2.40	2.61	3.40	3.69	2.47	2.93	3.12	3.01	3.16	3.55	-0.47	0.47
MPW1K	3.09	3.39	4.65	5.03	3.25	3.89	4.22	3.96	4.09	4.86	0.54	0.54
mPW1PW91	3.09	3.43	4.65	5.06	3.25	3.88	4.22	3.97	4.10	4.86	0.55	0.55
Average											0.10	0.24

[a] The aug-cc-pVTZ basis set are employed in all calculations in this table.
[b] Ref. [2] [c] Ref. [3]

Table 2: Binding energies (in kcal/mol) of rare-gas dimers without counterpoise correction for BSSE [a]

Method	He_2	Ne_2	Ar_2	Kr_2	HeNe	HeAr	HeKr	NeAr	NeKr	ArKr	MSE	MUE
Reference	0.022 [b]	0.084 [b]	0.285 [b]	0.400 [b]	0.041 [c]	0.057 [c]	0.057 [c]	0.134 [c]	0.142 [c]	0.361 [c]		
M05-2X	0.025	0.181	0.266	0.291	0.084	0.082	0.085	0.194	0.201	0.275	**0.010**	**0.053**
B97-1	0.072	0.124	0.185	0.224	0.100	0.099	0.101	0.144	0.152	0.201	**-0.018**	**0.069**
B98	0.051	0.089	0.121	0.148	0.072	0.067	0.068	0.100	0.105	0.132	-0.063	**0.080**
PBE	0.075	0.128	0.138	0.163	0.104	0.090	0.090	0.136	0.144	0.149	-0.037	**0.082**
PBEPW91	0.077	0.132	0.145	0.172	0.107	0.093	0.094	0.141	0.150	0.157	**-0.032**	**0.083**
M05	0.075	0.199	0.225	0.232	0.131	0.110	0.091	0.215	0.198	0.220	**0.011**	0.085
PBE1W	0.079	0.132	0.135	0.158	0.108	0.093	0.093	0.138	0.146	0.145	-0.036	0.086
PBE0	0.042	0.080	0.092	0.109	0.064	0.054	0.052	0.084	0.086	0.099	-0.082	0.091
PWB6K	0.150	0.269	0.271	0.309	0.177	0.188	0.154	0.240	0.174	0.291	0.064	0.099
TPSS	0.047	0.085	0.072	0.079	0.071	0.052	0.055	0.077	0.084	0.076	-0.089	0.100
PW6B95	0.095	0.189	0.132	0.206	0.148	0.133	0.125	0.190	0.166	0.202	**0.000**	0.101
MPWB1K	0.048	0.102	0.012	0.093	0.071	0.048	0.048	0.088	0.093	0.095	-0.089	0.103
TPSSh	0.039	0.073	0.064	0.070	0.061	0.044	0.046	0.066	0.072	0.067	-0.098	0.105
MPW1B95	0.057	0.116	-0.004	0.089	0.081	0.052	0.057	0.096	0.106	0.093	-0.084	0.105
mPW1PW91	0.038	0.069	0.053	0.050	0.055	0.043	0.040	0.064	0.065	0.052	-0.105	0.111
MPW1K	0.027	0.052	0.042	0.040	0.042	0.032	0.029	0.049	0.048	0.041	-0.118	0.119
PW91	0.231	0.337	0.305	0.324	0.284	0.250	0.251	0.335	0.347	0.314	0.139	0.164
LSDA	0.227	0.528	0.761	0.895	0.369	0.363	0.353	0.606	0.627	0.818	0.396	0.396
Average											-0.01	0.11

[a] The aug-cc-pVTZ basis set are employed in all calculations in this table.
[b] Ref. [2] [c] Ref. [3]

Table 3: Binding energies (in kcal/mol) of rare-gas dimers with counterpoise correction for BSSE [a b]

Method	He_2	Ne_2	Ar_2	Kr_2	HeNe	HeAr	HeKr	NeAr	NeKr	ArKr	MSE	MUE
Reference	0.022 [b]	0.084 [b]	0.285 [b]	0.400 [b]	0.041 [c]	0.057 [c]	0.057 [c]	0.134 [c]	0.142 [c]	0.361 [c]		
M05-2X	0.021	0.151	0.238	0.261	0.069	0.074	0.066	0.171	0.170	0.248	**-0.012**	**0.048**
B97-1	0.071	0.105	0.171	0.208	0.091	0.095	0.095	0.131	0.139	0.187	**-0.029**	**0.068**
PBEPW91	0.075	0.115	0.134	0.155	0.098	0.088	0.087	0.130	0.138	0.143	-0.042	**0.082**
PBE	0.073	0.111	0.127	0.146	0.095	0.085	0.084	0.125	0.133	0.136	-0.047	**0.084**
B98	0.049	0.070	0.109	0.133	0.062	0.062	0.063	0.087	0.093	0.119	-0.074	**0.086**
M05	0.074	0.165	0.198	0.204	0.118	0.107	0.103	0.193	0.195	0.196	**-0.003**	0.086
PBE1W	0.077	0.116	0.125	0.142	0.099	0.088	0.087	0.128	0.136	0.133	**-0.045**	0.086
PWB6K	0.149	0.246	0.259	0.301	0.167	0.184	0.148	0.228	0.168	0.283	0.055	0.095
PBE0	0.041	0.062	0.081	0.095	0.054	0.049	0.041	0.071	0.075	0.086	-0.093	0.099
PW6B95	0.094	0.174	0.118	0.196	0.139	0.130	0.122	0.178	0.160	0.193	**-0.008**	0.100
TPSS	0.045	0.068	0.061	0.065	0.059	0.049	0.049	0.068	0.074	0.063	-0.098	0.107
MPWB1K	0.047	0.085	-0.004	0.082	0.060	0.043	0.046	0.075	0.086	0.084	-0.098	0.107
MPW1B95	0.056	0.099	-0.019	0.077	0.070	0.048	0.055	0.083	0.100	0.082	-0.093	0.109
TPSSh	0.038	0.056	0.052	0.057	0.049	0.041	0.037	0.057	0.062	0.055	-0.108	0.113
mPW1PW91	0.037	0.060	0.042	0.040	0.049	0.038	0.037	0.055	0.057	0.042	-0.113	0.117
MPW1K	0.026	0.041	0.031	0.031	0.034	0.027	0.027	0.039	0.040	0.031	-0.126	0.127
PW91	0.229	0.315	0.293	0.307	0.273	0.245	0.244	0.320	0.333	0.300	0.128	0.158
LSDA	0.224	0.491	0.714	0.827	0.349	0.345	0.334	0.566	0.583	0.763	0.361	0.361
Average											-0.02	0.11

[a] The aug-cc-pVTZ basis set are employed in all calculations in this table.
Ref. [2] [c] Ref. [3]

Table 4: Bond lengths (in Å) of alkaline metal dimers, Zn_2, and Zn-rare-gas dimers without counterpoise correction for BSSE [a b]

Method	Be_2	Mg_2	Ca_2	Zn_2	ZnNe	ZnAr	ZnKr	MSE	MUE
Reference	2.45	3.89	4.28	4.19	4.42	4.38	4.20		
PWB6K	2.62	3.79	4.30	3.67	4.00	4.25	4.28	-0.13	**0.21**
M05-2X	2.66	3.86	4.41	3.85	3.93	4.27	4.38	**-0.06**	**0.21**
B98	2.53	3.68	4.26	3.51	3.99	4.36	4.47	-0.15	**0.25**
PW6B95	2.52	3.74	4.23	3.58	4.12	4.63	4.55	**-0.06**	**0.25**
B97-1	2.52	3.63	4.23	3.48	3.86	4.20	4.32	-0.22	**0.28**
MPWB1K	2.61	3.75	4.28	3.62	4.20	4.66	4.78	**0.01**	0.28
PBE0	2.50	3.59	4.20	3.32	4.06	4.45	4.53	-0.17	0.29
MPW1B95	2.54	3.70	4.23	3.52	4.17	4.65	4.78	**-0.03**	0.30
M05	2.54	3.63	4.23	3.55	3.57	4.11	4.25	-0.28	0.32
PBE1W	2.42	3.56	4.12	3.30	3.89	4.38	4.49	-0.23	0.32
PBE	2.42	3.50	4.10	3.17	3.87	4.28	4.38	-0.30	0.35
PBEPW91	2.42	3.51	4.10	3.18	3.85	4.25	4.34	-0.31	0.35
PW91	2.42	3.50	4.09	3.14	3.77	4.23	4.35	-0.33	0.37
TPSSh	2.47	3.55	4.15	3.18	4.23	4.75	4.99	**-0.07**	0.41
TPSS	2.44	3.51	4.11	3.10	4.19	4.72	4.88	-0.12	0.41
MPW1K	2.58	3.66	4.27	3.45	4.56	5.11	5.30	0.16	0.44
mPW1PW91	2.51	3.60	4.21	3.34	4.41	5.09	5.31	0.09	0.44
LSDA	2.40	3.40	3.99	2.85	3.19	3.51	3.60	-0.70	0.70
Average								-0.16	0.34

[a] The aug-CV(T+2d)Z (see text) is employed for Ca, and the aug-cc-pVTZ basis set is employed for all other elements.
[b] The reference data for Be_2: ref.[51]; Mg_2: ref. [34];Ca_2: ref. [35]; Zn_2:[47]; ZnNe: ref. [79]; ZnAr: ref. [60]; ZnKr: ref. [80].

Table 5: Binding energies (in kcal/mol) of alkaline metal dimers and Zn_2 without counterpoise correction for BSSE [a]

Method	X [b]	Be_2	Mg_2	Ca_2	Zn_2	MSE	MUE
Reference		2.72 [c]	1.21 [c]	3.13 [c]	0.80 [c]		
M05-2X	56	2.53	1.20	2.90	0.77	**-0.12**	**0.12**
PWB6K	46	3.07	1.38	3.34	0.74	**0.17**	**0.20**
MPWB1K	44	3.08	1.30	3.36	0.53	**0.10**	**0.24**
PW6B95	28	4.36	1.38	3.57	0.66	**0.53**	**0.59**
MPW1B95	31	4.22	1.45	3.68	0.59	**0.52**	**0.62**
M05	28	4.53	1.39	3.49	1.07	0.65	0.65
MPW1K	43	4.33	1.98	4.04	0.76	0.81	0.83
B98	22	5.49	2.04	4.15	0.93	1.19	1.19
mPW1PW91	25	6.09	2.28	4.60	0.91	1.50	1.50
B97-1	21	6.20	2.41	4.65	1.19	1.65	1.65
PBE0	25	6.60	2.61	4.93	1.27	1.89	1.89
TPSSh	10	6.93	2.66	5.56	1.36	2.16	2.16
PBE1W	0	9.04	2.51	5.48	1.18	2.58	2.58
TPSS	0	8.17	2.97	6.27	1.63	2.80	2.80
PBEPW91	0	9.86	3.20	6.24	1.77	3.30	3.30
PBE	0	9.89	3.28	6.32	1.80	3.36	3.36
PW91	0	10.05	3.41	6.50	2.04	3.53	3.53
LSDA	0	12.93	5.00	7.91	5.25	5.81	5.81
Average						1.80	1.83

[a] The aug-CV(T+2d)Z (see text) is employed for Ca, and the aug-cc-pVTZ basis set is employed for all other elements.
[b] X denotes the percentage of Hartree-Fock exchange in the functional.
[c] The reference data for Be_2: ref.[51]; Mg_2: ref. [34];Ca_2: ref. [35]; Zn_2: ref.[47].

Table 6: Binding energies (in kcal/mol) of alkaline metal dimers and Zn_2 with counterpoise correction for BSSE [a]

Method	X [b]	Be_2	Mg_2	Ca_2	Zn_2	MSE	MUE
Reference		2.72 [c]	1.21 [c]	3.13 [c]	0.80 [c]		
M05-2X	56	2.45	1.13	2.87	0.72	**-0.17**	**0.17**
PWB6K	46	3.04	1.37	3.33	0.72	**0.15**	**0.19**
MPWB1K	44	3.06	1.28	3.35	0.51	**0.08**	**0.23**
PW6B95	28	4.30	1.35	3.55	0.64	**0.49**	**0.57**
M05	28	4.46	1.33	3.43	1.01	0.59	**0.59**
MPW1B95	31	4.18	1.42	3.66	0.57	**0.49**	0.61
MPW1K	43	4.24	1.93	4.03	0.75	0.77	0.80
B98	22	5.40	1.98	4.14	0.84	1.12	1.12
mPW1PW91	25	5.95	2.22	4.58	0.88	1.44	1.44
B97-1	21	6.10	2.35	4.64	1.16	1.60	1.60
PBE0	25	6.49	2.55	4.91	1.24	1.83	1.83
TPSSh	10	6.73	2.56	5.54	1.33	2.08	2.08
PBE1W	0	8.87	2.43	5.45	1.13	2.50	2.50
TPSS	0	7.92	2.86	6.25	1.60	2.69	2.69
PBEPW91	0	9.68	3.10	6.22	1.72	3.22	3.22
PBE	0	9.71	3.19	6.32	1.75	3.27	3.27
PW91	0	9.86	3.33	6.46	1.99	3.44	3.44
LSDA	0	12.81	4.77	7.89	5.16	5.69	5.69
Average						1.74	1.78

[a] The aug-CV(T+2d)Z (see text) is employed for Ca, and the aug-cc-pVTZ basis set is employed for all other elements.
[b] X denotes the percentage of Hartree-Fock exchange in the functional.
[c] The reference data for Be_2: ref.[51]; Mg_2: ref. [34];Ca_2: ref. [35]; Zn_2: ref.[47].

Table 7: Binding energies (in kcal/mol) of zinc-rare-gas dimers without counterpoise corrections for BSSE [a]

Method	ZnNe	ZnAr	ZnKr	MSE	MUE
Reference	0.067 [b]	0.234 [b]	0.329 [b]		
B97-1	0.158	0.236	0.284	**0.016**	**0.046**
M05-2X	0.101	0.200	0.245	**-0.028**	**0.050**
PWB6K	0.213	0.254	0.272	0.037	**0.074**
PBEPW91	0.177	0.193	0.227	**-0.011**	**0.084**
B98	0.112	0.159	0.192	-0.056	**0.085**
PBE	0.170	0.182	0.215	**-0.021**	0.089
M05	0.295	0.276	0.306	0.082	0.098
PBE1W	0.173	0.173	0.197	-0.029	0.099
PW6B95	0.194	0.188	0.193	**-0.018**	0.103
PBE0	0.086	0.111	0.135	-0.099	0.112
MPWB1K	0.091	0.095	0.099	-0.115	0.131
MPW1B95	0.111	0.103	0.104	-0.104	0.133
TPSS	0.096	0.083	0.090	-0.120	0.139
TPSSh	0.078	0.071	0.078	-0.134	0.142
mPW1PW91	0.073	0.055	0.053	-0.149	0.153
PW91	0.388	0.344	0.366	0.156	0.156
MPW1K	0.049	0.041	0.040	-0.167	0.167
LSDA	0.641	0.978	1.199	0.729	0.729
Average				-0.043	0.099

[a] The aug-cc-pVTZ basis set are employed for all calculations.
[b] The reference data for ZnNe: ref. [79]; ZnAr: ref. [60]; ZnKr: ref. [80]

Table 8: Binding energies (in kcal/mol) of zinc-rare-gas dimers with counterpoise corrections for BSSE [a]

Method	ZnNe	ZnAr	ZnKr	MSE	MUE
Reference	0.067 [b]	0.234 [b]	0.329 [b]		
B97-1	0.150	0.224	0.269	**0.004**	**0.051**
M05-2X	0.088	0.177	0.212	-0.051	**0.065**
PWB6K	0.207	0.246	0.263	**0.029**	**0.073**
B98	0.106	0.147	0.178	-0.066	**0.092**
PBEPW91	0.169	0.179	0.208	**-0.024**	**0.092**
M05	0.274	0.263	0.273	0.060	0.097
PBE	0.162	0.170	0.196	**-0.034**	0.097
PBE1W	0.166	0.161	0.180	-0.041	0.107
PW6B95	0.190	0.181	0.183	**-0.025**	0.107
PBE0	0.081	0.101	0.122	-0.109	0.118
MPWB1K	0.084	0.088	0.091	-0.122	0.134
MPW1B95	0.105	0.095	0.095	-0.112	0.137
PW91	0.379	0.329	0.346	0.142	0.142
TPSS	0.089	0.072	0.075	-0.131	0.145
TPSSh	0.071	0.061	0.065	-0.144	0.147
mPW1PW91	0.068	0.047	0.043	-0.157	0.157
MPW1K	0.044	0.033	0.032	-0.173	0.173
LSDA	0.604	0.936	1.134	0.681	0.681
Average				-0.015	0.145

[a] The aug-cc-pVTZ basis set are employed for all calculations.
[b] The reference data for ZnNe: ref. [79]; ZnAr: ref. [60]; ZnKr: ref. [80]

Table 9: Mean percentage unsigned errors (M%UE) [a]

Method	Energetics										Geometry			MMMM%UE
	Rare Gas Dimers			Metal Dimers			Zn-rare-gas dimers			MMM%UE	Bond Length			
	no-CP	CP	MM%UE	no-CP	CP	MM%UE	no-CP	CP	MM%UE		no-CP	CP	MM%UE	
M05-2X	**49**	**34**	**41**	**5**	**9**	**7**	**30**	**30**	**30**	**26**	**5**	**5**	**5**	**16**
MPWB1K	58	**59**	**59**	**15**	**15**	**15**	55	53	54	**42**	6	6	6	**24**
B98	**49**	**51**	**50**	55	50	52	**47**	**47**	**47**	**50**	**5**	**5**	**5**	**27**
MPW1B95	63	63	63	**29**	29	**29**	63	62	63	**51**	6	6	6	**29**
B97-1	66	60	63	81	78	79	**50**	**49**	**49**	64	**5**	**5**	**5**	**34**
PBE0	**49**	**55**	**52**	94	90	92	**46**	**46**	**46**	**64**	5	6	6	35
MPW1K	62	69	66	39	38	38	66	70	68	58	13	14	14	36
mPW1PW91	60	64	62	68	65	66	56	56	56	61	13	14	14	37
PW6B95	114	108	111	**26**	**26**	**26**	83	83	83	73	**5**	**5**	**5**	39
TPSSh	**57**	62	60	106	101	103	**54**	**53**	**54**	72	9	10	9	41
M05	97	89	93	32	**27**	29	121	112	116	78	7	7	7	42
PWB6K	169	161	165	**10**	**10**	**10**	81	78	79	84	**5**	**5**	**5**	45
PBE1W	73	69	71	115	111	113	74	74	74	86	6	6	6	46
TPSS	**56**	**59**	**58**	138	132	135	60	59	60	84	9	9	9	46
PBEPW91	72	66	69	162	157	159	70	70	70	99	6	6	6	53
PBE	68	65	67	165	160	163	70	69	69	100	6	6	6	53
PW91	283	273	278	166	148	157	178	167	172	201	6	6	6	103
LSDA	458	428	443	350	341	345	478	447	462	412	15	15	15	213
Average	106	102	104	92	88	90	93	90	92	95	7	8	7	51

[a] see section 3.6 for the definitions of MM%UE, MMM%UE, and MMMM%UE. CP denotes the counterpoise correction for BSSE.

Table 10: Mean unsigned errors (kcal/mol) on a broad range of energetic databases.

Functional	WI17 [a]	NCBE31	TMAE4/05 [b]	MLBE4/05 [b]	MGT135	HTK57	NHTBH38	AMUEXM [c]	AMUE [d]
M05-2X	**0.07**	**0.3** [b]	29.4	15.2	**0.9** [b]	**1.0** [b]	**1.7** [a]	**0.8**	7.0
MPWB1K	**0.14**	**0.6** [e]	29.3	11.5	1.4 [f]	**1.3** [b]	**1.5** [g]	**1.0**	6.5
B98	0.34	0.8 [e]	**19.9**	8.0	**1.0** [f]	2.6 [b]	3.4 [g]	1.6	**5.1**
MPW1B95	0.23	0.7 [e]	25.1	7.6	**1.0** [e,f]	1.9 [b]	2.3 [g]	**1.2**	5.5
B97-1	0.43	0.7 [e]	**18.6**	8.4	1.1 [e]	2.9 [b,f]	3.5 [g]	1.7	**5.1**
PBE0	0.51	0.7 [e]	25.0	**6.3**	1.3 [e,f]	2.8 [b]	3.5 [g]	1.8	5.7
MPW1K	0.29	0.9 [e]	31.8	13.1	2.6 [e,f]	**1.3** [b]	**1.8** [g]	1.4	7.4
mPW1PW91	0.44	1.0 [e]	26.5	**7.0**	1.3 [e,f]	2.3 [f]	3.2 [g]	1.7	6.0
PW6B95	**0.22**	**0.6** [e]	**24.3**	**7.4**	**0.8** [f]	2.0 [a]	2.9 [a]	1.3	**5.5**
TPSSh	0.59	1.1 [e]	**16.0**	**4.6**	1.4 [f]	4.3 [b,f]	6.9 [g]	2.8	**5.0**
M05	**0.21**	**0.5** [h]	**7.3**	**5.0**	**1.0** [h]	**1.4** [b,f]	**2.1** [g]	**1.1**	**2.5**
PWB6K	**0.12**	**0.4** [f]	33.9	13.6	1.7 [e]	**1.4** [b,f]	**1.4** [a]	**1.0**	7.5

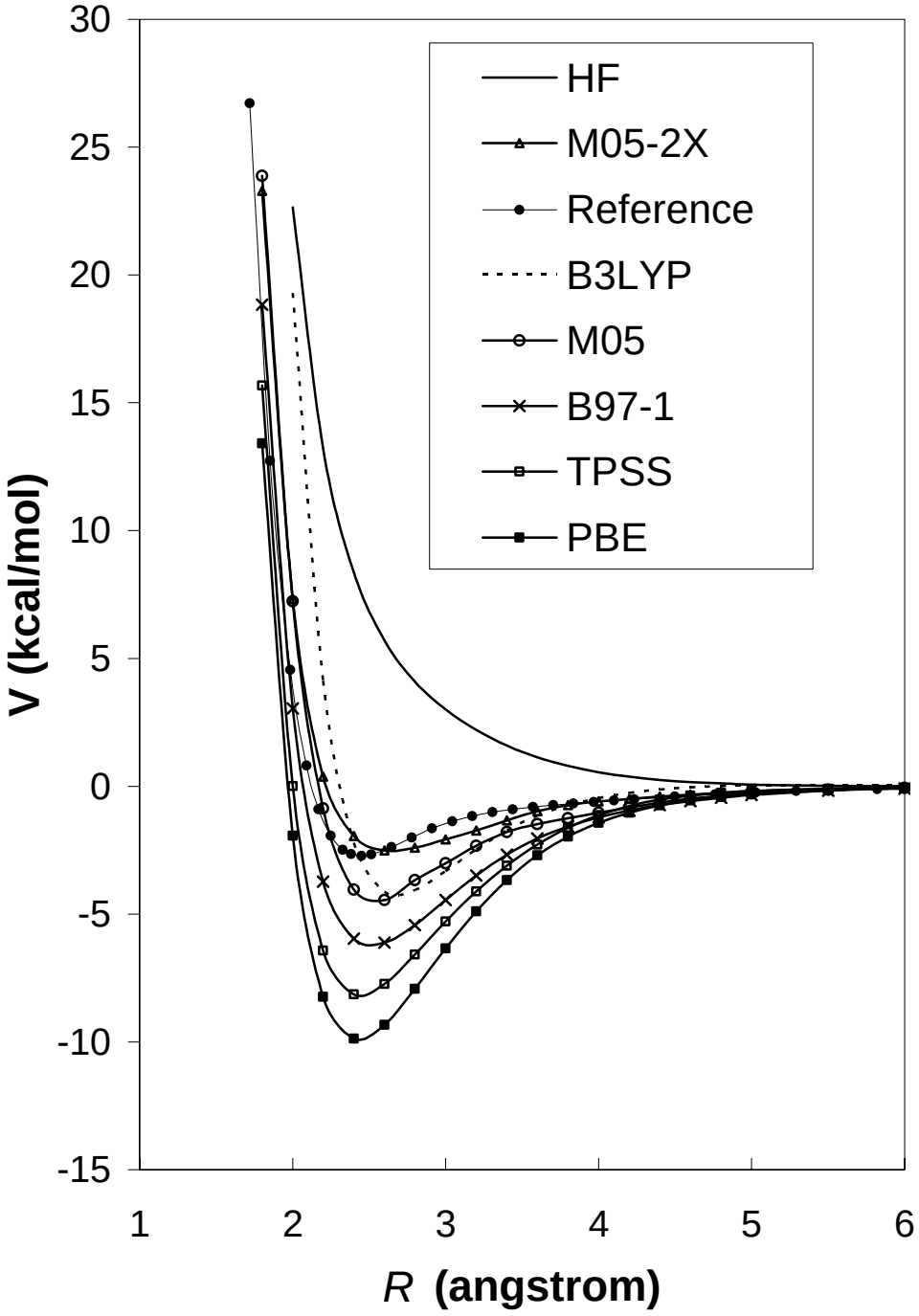
[a] present work
[b] Ref. [57]
[c] Average over mean errors for the WI17, NCBE31, MGT135, HTK57, and NHTBH databases.
[d] Average over mean errors for all seven databases.
[e] Ref. [53]
[f] Ref. [24]
[g] Ref. [96]
[h] Ref. [56]

Figure captions

Figure 1. Potential energy curves for the Be_2 dimer. The aug-cc-pVTZ basis set is used for all calculations in this figure, and no counterpoise corrections are applied. The reference curve is taken form Ref.51.

Figure 2. Potential energy curves for the Ar_2 dimer. The aug-cc-pVTZ basis set is used for all calculations in this figure, and no counterpoise corrections are applied.

Figure 1.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20
15
10
5
0
-5
-10
-15
1
2
3
4
5
6
V (kcal/mol)
R (angstrom)
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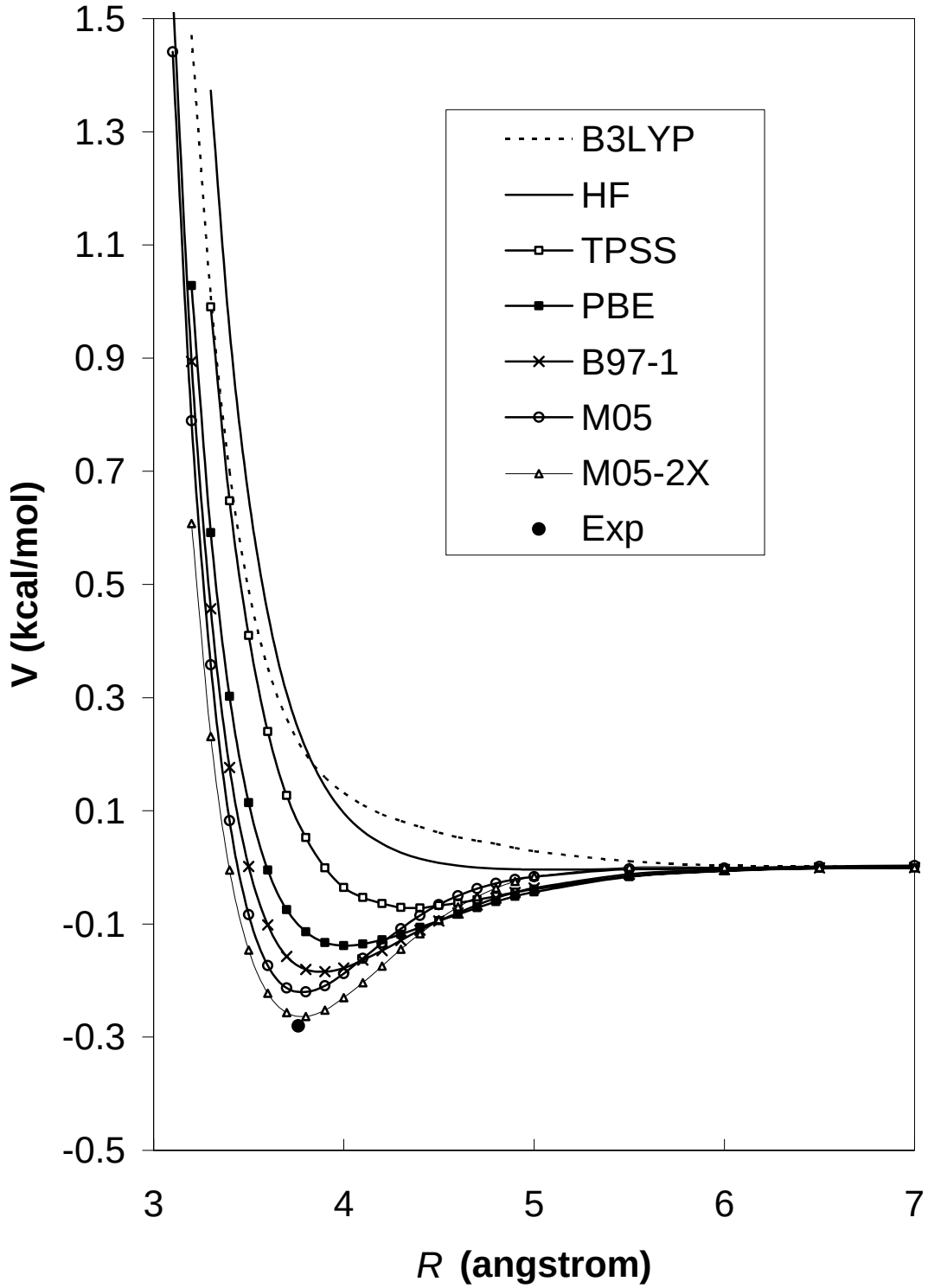
M05-2X
Reference
B3LYP
M05
B97-1
TPSS
PBE

Figure 2.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0.7
0.5
0.3
0.1
-0.1
-0.3
-0.5
V (kcal/mol)
3
4
5
6
7
R (angstrom)
B3LYP
HF
TPSS
PBE
B97-1
M05
M05-2X
Exp