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Multi-Coefficient Extrapolated DFT Studies of $\pi\cdots\pi$ Interactions: The Benzene Dimer

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Abstract.

We report tests of new (2005) and established (1999-2003) multi-level methods against essentially converged benchmark results for nonbonded $\pi\cdots\pi$ interactions in benzene dimers. We found that the newly developed multi-coefficient extrapolated density function theory (DFT) methods (which combine DFT with correlated wave function methods) give better performance than multilevel methods such as G3SX, G3SX(MP3) and CBS-QB3 that are based purely on wave function theory (WFT); furthermore they have a lower computational cost. We conclude that our empirical approach for combining WFT methods with DFT methods is a very efficient and effective way for describing not only covalent interactions (as shown previously) but also nonbonded interactions.

Among the various types of nonbonded interactions between molecules, $\pi\cdots\pi$ interactions are increasingly singled out for the key roles they play in molecular recognition, protein folding, stacking of nucleobases, intercalation of drugs into DNA, nonlinear optical materials, crystal packing, self-assembly, solvation, and supramolecular chemistry.¹⁻²⁸ Benzene dimer is of key importance as a prototype of aromatic $\pi\cdots\pi$ interactions, and it has been extensively studied both experimentally⁹ and theoretically.^{2,9,10,14,15,23-25} Due to the weakness (~ 2 - 3 kcal/mol) and anharmonicity of the benzene-benzene interaction, it is difficult to extract the binding energy of benzene dimer from experiment. Theoretically, it is prohibitive to perform a reasonably converged calculation (for example, W1²⁹ or other large-basis-set CCSD(T)³⁰ calculation) for these dimers, but one can afford to calculate second-order Møller-Plesset perturbation³¹ (MP2) method with a large basis set. Unfortunately the difference between MP2 and CCSD(T) binding energy for benzene dimers is about 1-2 kcal/mol;¹⁵ therefore it is essential to include the CCSD and (T) contributions for benzene dimer calculations. The “standard” approach is to combine MP2 theory in the complete basis set (CBS) limit with a Δ CCSD(T) correction computed in a smaller basis (for example, a polarized double zeta basis set) to estimate the CBS CCSD(T) results.^{15,17,24}

Recently we developed a suite of new methods by empirically combining wave function theory (WFT) methods with density functional theory (DFT) methods; the combination methods are called multi-coefficient extrapolated DFT methods.³² In these methods, we use small basis sets for higher-level methods to obtain the correlation contributions, and we use large basis sets for lower-level methods to do basis set extrapolation. Instead of simply adding these contributions together, we used empirical parameters to scale these energy components to approximate complete configuration interaction calculations (CCI). These methods were parametrized against a data set for thermochemistry and thermochemical kinetics. One can think of these new methods as improving the exact-exchange part of the hybrid DFT method, or one can think of them as adding static

correlation³³ (as contained in the DFT exchange functional) to the best practical single-reference WFT methods.

In the present communication, we will show that these multi-coefficient extrapolated DFT methods are accurate not only for thermochemistry, which is dominated by covalent interactions, and thermochemical kinetics, which involve partial bonds, but also for benzene dimer interactions, which are dominated by dispersion forces. This is particularly noteworthy because these methods³² were only trained against a dataset for covalent interactions. In particular the present letter gives the results calculated by the multi-coefficient extrapolated DFT methods that scale N^6 and N^7 (where N is the number of atoms). We tested three N^7 methods, namely MCG3-MPW, MCG3-MPWB, and MCG3-TS, and we tested six N^6 methods, namely MCQCISD-MPW, MCQCISD-MPWB, MCQCISD-TS, MCUT-MPW, MCUT-MPWB, and MCUT-TS. In the name of these methods, we used the same notation as in the original paper:³²

MPW: mPW exchange³⁴ + PW91 correlation³⁵

MPWB: mPW exchange³⁴ + B95 correlation³⁶

TS: TPSS exchange³⁷ + KCIS correlation³⁸

The energy functions and coefficient trees for these tested methods are described in a previous paper.³²

We compare the results obtained by the multi-coefficient extrapolated DFT methods to those obtained by the pure-WFT-based multi-level methods in particular, G3SX,³⁹ CBS-QB3,⁴⁰ and MCCM/3,⁴¹ and G3SX(MP3).³⁹ Within the MCCM/3 suite, we specifically consider MCG3/3, MC-QCISD/3, and MC-UT/3. We also compare our results to the very accurate calculations by Sinnokrot and Sherrill²⁴ and to results obtained by the Aromatic Inter-Molecular Interaction (AIMI) model by Tsuzuki et al.¹⁴

All the calculations in the present study are performed by using locally developed program *MLGAUSS*⁴² in conjunction with *Gaussian03*.⁴³ The *MLGAUSS* program is available from the Truhlar group's software webpage.⁴⁴ The geometries for the benzene dimers are taken

from Sinnokrot and Sherrill,²⁴ who optimized them at the estimated CCSD(T)/aug-cc-pVQZ* level of theory using frozen monomers (C-C bond distance of 1.3915 Å and C-H bond distance of 1.0800 Å). The aug-cc-pVQZ* basis is an aug-cc-pVQZ basis^{45,46} minus all *g* functions on carbon and minus all *f* functions on hydrogen. The estimated CCSD(T)/ aug-cc-pVQZ* energy was obtained by the equation

$$E_{\text{CCSD(T)}}^{\text{aug-cc-pVQZ}^*}(\text{est.}) = E_{\text{MP2}}^{\text{aug-cc-pVQZ}^*} + \Delta\text{CCSD(T)} \quad (1)$$

where $\Delta\text{CCSD(T)}$ correction is computed in an aug-cc-pVDZ* basis as

$$\Delta\text{CCSD(T)} = E_{\text{CCSD(T)}}^{\text{aug-cc-pVDZ}^*} - E_{\text{MP2}}^{\text{aug-cc-pVDZ}^*} \quad (2)$$

where aug-cc-pVDZ* is a basis that uses aug-cc-pVDZ on carbon and cc-pVDZ on hydrogen.

Figure 1 shows the three conformers of benzene dimer: sandwich (S), T-shaped (T), and parallel-displaced (PD). Note that, energetically, PD is the global minimum, T is a local minimum, and S is a saddle point.

Table 1 gives the results for the N^7 methods. In the table, we used the estimated CCSD(T) CBS results (that is the estimate of the complete basis set limit of CCSD(T)) of Sinnokrot et al¹⁵ as the best estimate. We also tabulated the mean signed error (MSE, where signed error (SE) = calculation – best estimate) and mean unsigned error (MUE, the same as mean absolute deviation). The costs of the methods are measured in a standard way that we have used many times, as described in a previous paper³² and in a footnote to the table.

Table 1 shows that the three N^7 multi-coefficient extrapolated DFT methods, namely MCG3-TS, MCG3-MPWB, and MCG3-MPW, outperform CBS-QB3, G3SX(MP3), and G3SX by a large margin with less computer cost. Note that the cost of G3SX is about an order of magnitude higher than the three N^7 multi-coefficient extrapolated methods. In a previous paper we have shown that MCG3-TS, MCG3-MPWB, and MCG3-MPW also outperform G3SX for covalent interactions. Combining that result with the present finding, we conclude that our empirical hybrids of DFT methods with WFT methods are suitable not only for covalent interactions, but also for nonbonded interactions, although our methods were only

parametrized against a data set for covalent interactions. Table 1 also shows that the qualities of MCG3-TS, and MCG3-MPWB, and MCG3-MPW for the benzene dimer interactions are comparable (the same for MCG3-TS and 0.04-0.05 kcal/mol worse for the other two methods) to that of the estimated CCSD(T)/aug-cc-PVQZ* calculation, and they are better than the AIMI models of Tsuzuki et al.,¹⁴ which is specifically developed for this kind of problem.

Table 2 shows that the three N^6 multi-coefficient extrapolated methods based on MC-QCISD/3,⁴¹ namely MCQCISD-TS, MCQCISD-MPWB, and MCQCISD-MPW, outperform the three N^6 multi-coefficient extrapolated methods based on MC-UT/3,⁴¹ namely MCUT-TS, MCUT-MPWB, and MCUT-MPW, by a large margin with slightly more computer cost. This result shows that the QCISD contribution (which is included in MCQCISD methods but not in MCUT methods) is essential for describing these benzene dimer interactions for the multi-coefficient extrapolated methods. (CCSD would be expected to be just as good as or better than QCISD.) Note that the performance of MCQCISD-MPWB is comparable to the best N^7 methods, and it is about two magnitudes less expensive than the G3SX method (with the standard function and even more relative cost efficient for larger systems like the benzene dimer). One encouraging point from Table 2 is that the highest level of calculation in MCQCISD-MPWB is QCISD/6-31G(d), which scales as N^6 , so MCQCISD-MPWB can be applied to systems where N^7 methods are prohibitive. The N^6 single-level ab initio method, CCSD/aug-cc-pVDZ, is less accurate and computationally more expensive than all other N^6 multi-level methods in the table. Comparing the results in Table 1 to those in Table 2, we can see that even though the performance of MCUT-MPWB is not satisfactory, it still outperforms the much more expensive N^7 method, CBS-QB3. Note that for covalent interactions, MCQCISD-TS gives better performance than MCQCISD-MPWB,³² but for benzene dimer interactions MCQCISD-MPWB is better. This is consistent with our previous finding that mPW³⁴ exchange and B95³⁶ correlation is a good combination of DFT functionals for nonbonded interactions,^{47,48} for example, MPW1B95⁴⁷ and MPWB1K⁴⁷ outperform TPSS1KCIS³² and mPW1PW91³⁴ for weak interactions.

Calculating the interaction energy of benzene dimers is a critical test of electronic structure theory. Summarizing the results in Tables 1 and 2 and the results for covalent interactions in a previous paper,³² we conclude that our empirical approach to combining WFT methods with DFT methods is a very efficient and effective way for describing both covalent interactions and nonbonded interactions.

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Table 1. Binding energies (kcal/mol), mean errors (kcal/mol), and cost for N^7 methods ^{a b}

Method	S	T	PD	MSE	MUE	Cost	Ref.
Best Estimate	1.81	2.74	2.78	-	-	-	¹⁵
MCG3-TS	1.60	2.81	2.88	-0.01	0.13	46.2	This Work
MCG3-MPWB	1.49	2.84	2.88	-0.04	0.17	46.2	This Work
MCG3-MPW	1.66	2.92	3.00	0.08	0.18	46.1	This Work
CBS-QB3	2.59	3.45	3.88	0.86	0.86	55.0	This Work
G3SX(MP3)	2.95	3.85	4.35	1.27	1.27	66.0	This Work
MCG3/3	2.92	3.83	4.46	1.30	1.30	45.0	This Work
G3SX	2.98	3.89	4.35	1.30	1.30	460	This Work
estd. CCSD(T)/aug-cc-pVQZ* ^c	1.70	2.61	2.63	-0.13	0.13	2200	²⁴
AIMI-I ^d	1.54	2.36	2.60	-0.28	0.28	-	¹⁴
AIMI-II ^d	1.62	2.42	2.59	-0.23	0.23	-	¹⁴
AIMI-III ^d	1.48	2.46	2.48	-0.30	0.30	-	¹⁴

^a S: sandwich; T: T-shaped; PD: parallel displaced (Figure 1). MSE: mean signed error; MUE: mean unsigned error = mean absolute deviation.

^b Cost is a standard cost measure that we have defined and used previously, namely the sum of the times to calculate the gradients for the two molecules, 1-phosphinomethanol and 2,2-dichloro-1-ethanol, divided by the sum of the times for MP2/6-31G(2df,p) gradient calculations on the same computer. For the present paper the computer used is a single 500MHZ processor of an SGI origin 3800.

^c aug-cc-pVQZ* is the aug-cc-pVQZ basis minus all *g* function on carbon and all *f* function on hydrogen. The cost of this method is estimated as the sum of the cost of each level involved.

^d See reference ¹⁴ for the AIMI-I, AIMI-II, and AIMI-III methods.

Table 2. Binding energies (kcal/mol), mean errors (kcal/mol), and cost for N^6 methods

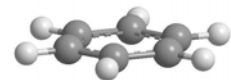
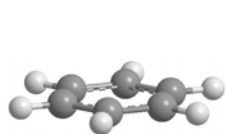
Method	S	T	PD	MSE	MUE	Cost
MCQCISD-MPWB	1.37	2.69	2.77	-0.17	0.17	6.0
MCQCISD-MPW	1.25	2.56	2.53	-0.33	0.33	6.0
MCQCISD-TS	1.25	2.49	2.46	-0.38	0.38	6.0
MCUT-MPWB	0.83	2.29	2.16	-0.68	0.68	5.5
MCUT-TS	0.76	2.11	1.87	-0.86	0.86	5.5
MCUT-MPW	0.62	2.07	1.77	-0.96	0.96	5.5
MC-UT/3	2.79	3.71	4.30	1.16	1.16	5.3
MCQCISD/3	3.02	3.79	4.57	1.35	1.35	5.5
CCSD/aug-cc-pVDZ	2.71	4.70	4.26	1.45	1.45	10.5

^a See the footnotes of Table 1 for the description of S, T, PD, MSE, MUE, and cost.

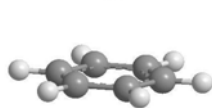
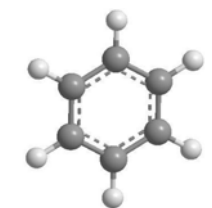
Figure caption:

Figure 1. Sandwich, T-shaped, and parallel-displaced conformers of benzene dimer.

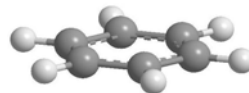
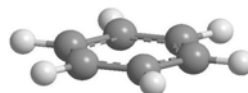
Figure 1



Sandwich (S)



T-shaped (T)



Parallel-displaced (PD)

