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Multicoefficient Extrapolated Density Functional Theory Studies of $\pi\cdots\pi$ Interactions: The Benzene Dimer

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We report tests of new (2005) and established (1999−2003) multilevel methods against essentially converged benchmark results for nonbonded interactions in benzene dimers. We found that the newly developed multicoefficient extrapolated density functional 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.[1−29] The benzene dimer is of key importance as a prototype of aromatic $\pi\cdots\pi$ interactions, and it has been extensively studied both experimentally[9] and theoretically.[2,9,10,14,15,23−26] 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, W1[30] or other large-basis-set CCSD(T)[31] calculation) for these dimers, but one can afford to calculate second-order Mller−Plesset perturbation[32] (MP2) method with a large basis set. Although MP2 and CCSD(T) give nearly identical results for some $\pi\cdots\pi$ interaction dimers such as in the acetylene dimer, the difference between MP2 and CCSD(T) binding energy for benzene dimers is about 1−2 kcal/mol,[15] indicating that the highly delocalized or aromatic-type $\pi\cdots\pi$ interactions are very different from other $\pi\cdots\pi$ interactions; 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 CCSD(T) correction computed in a smaller basis (for example, a polarized double-ζ 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 multicoefficient extrapolated DFT methods.[33] 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. In general, one can think of these new methods as improving the exact-exchange and dynamical correlation of the hybrid DFT method, or one can think of them as adding static correlation[34] to the best practical single-reference WFT methods. Note that even though most standard DFT methods fail for systems with strong static correlation, the exchange part of the DFT functionals does contain some kinds of static correlation as explained by Gritsenko et al.,[35] Handy and Cohen,[36] and He et al.[37] For the specific case of dispersion, one must also have a reasonable treatment of dynamical correlation because dispersion interactions are intrinsically a dynamical correlation effect.

In the present communication, we will show that these multicoefficient extrapolated DFT methods are accurate not only for thermochemistry, which is dominated by covalent and other types of bonding interactions, and thermochemical kinetics, which involves partial bonds, but also for benzene dimer interactions, which are dominated by dispersion forces. This is particularly noteworthy because these methods[33] were only trained against a dataset for covalent interactions. In particular, the present letter gives the results calculated by the multicoefficient extrapolated DFT methods that scale asymptotically 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:[33]

MPW: mPW exchange[38] + PW91 correlation[39]

MPWB: mPW exchange[38] + B95 correlation[40]

TS: TPSS exchange[41] + KCIS correlation[42]

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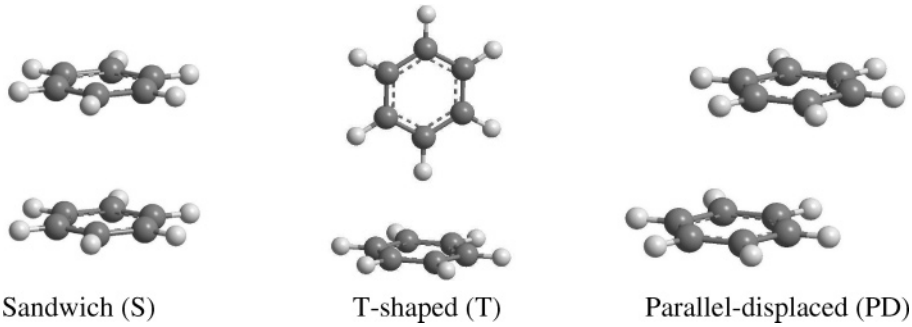

Figure 1. Sandwich, T-shaped, and parallel-displaced conformers of benzene dimer.

TABLE 1: Binding Energies (kcal/mol), Mean Errors (kcal/mol), and Cost for N^7 Methods[a,b]

						max. error			
method	S	T	PD	MSE	MUE	Error[c]	dimer[d]	cost	ref
best estimate	1.81	2.74	2.78						15
MCG3-TS	1.60	2.81	2.88	−0.01	0.13	−0.21	S	111	this work
MCG3-MPWB	1.49	2.84	2.88	−0.04	0.17	−0.32	S	111	this work
MCG3-MPW	1.66	2.92	3.00	0.08	0.18	0.22	PD	110	this work
CBS-QB3	2.59	3.45	3.88	0.86	0.86	1.10	PD	204	this work
G3SX(MP3)	2.95	3.85	4.35	1.27	1.27	1.57	PD	135	this work
MCG3/3	2.92	3.83	4.46	1.30	1.30	1.68	PD	104	this work
G3SX	2.98	3.89	4.35	1.30	1.30	1.57	PD	1116	this work
estd CCSD(T)/aug-cc-pVQZ*[e]	1.70	2.61	2.63	−0.13	0.13	−0.15	PD	1708	24
AIMI-I[f]	1.54	2.36	2.60	−0.28	0.28	−0.38	T		14
AIMI-II [f]	1.62	2.42	2.59	−0.23	0.23	−0.32	T		14
AIMI-III[f]	1.48	2.46	2.48	−0.30	0.30	−0.33	S		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 the time to calculate the single-point energy of the T-shaped benzene dimer (at the fixed geometry of Sinnokrot and Sherrill[24]) divided by the time for an MP2/6-311+G(2df,2p) single-point energy calculation for the same dimer on the same computer. For these timings the computer code is *Gaussian03*, the computer used is a single 1.7 GHz processor of an IBM Power4 supercomputer, and the calculations were carried out using a semidirect algorithm with a memory allocation for each job of 800 Megabytes. [c] Error = calculation − best estimate. [d] This is the dimer that gives the maximum error. [e] aug-cc-PVQZ* is the aug-cc-pVQZ basis minus all g functions on carbon and all f functions on hydrogen. The cost of this method is estimated as the sum of the cost of each level involved. [f] See ref 14 for the AIMI-I, AIMI-II, and AIMI-III methods.

The energy functions and coefficient trees for these tested methods are described in a previous paper.[33]

We compare the results obtained by the multicoefficient extrapolated DFT methods to those obtained by pure-WFT-based multilevel methods in particular, G3SX,[43] CBS-QB3,[44] MCCM/3,[45] and G3SX(MP3).[43] Within the MCCM/3 suite, we specifically consider MCG3/3, MC-QCISD/3, and MC-UT/3. Note that the zero-point corrections were excluded from the G3SX, G3SX(MP3), and CBS-QB3 calculations because, in the standard spectrospic notation, we are interested in predicting D_e, not D_0. We also compare our results to the very accurate calculations by Sinnokrot and Sherrill[24] and to results obtained by the Aromatic Intermolecular Interaction (AIMI) model by Tsuzuki et al.[14] Because the multicoefficient extrapolated DFT methods, MCCM/3, G3SX, G3SX(MP3), and CBS-QB3 were designed without counterpoise corrections, we do not include them in the present study.

All the calculations in the present study are performed by using the locally developed program *MLGAUSS*[46] in conjunction with *Gaussian03*.[47] The *MLGAUSS* program is available from the Truhlar group's software webpage.[48] 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 and C−H bond distance of 1.0800). The aug-cc-pVQZ* basis is an aug-cc-pVQZ basis[49,50] 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

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

where CCSD(T) correction is computed in an aug-cc-pVDZ* basis as

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

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 al.[15] 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 by the computer time for a single-point energy calculation of the T-shaped benzene dimer (at the fixed geometry of Sinnokrot and Sherrill[24]) divided by the computer time for an MP2/6-311+G(2df,2p) energy calculation on the same dimer with the same computer program and same computer.

Table 1 shows that the three N^7 multicoefficient 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 an order of magnitude higher than the three N^7 multicoefficient extrapolated methods. In a previous paper we have shown that MCG3-TS, MCG3-MPWB, and MCG3-MPW also outperform

TABLE 2: Binding Energies (kcal/mol), Mean Errors (kcal/mol), and Cost for N^6 Methods[a]

						max. error		
method	S	T	PD	MSE	MUE	error[b]	dimer[c]	cost
MCQCISD-MPWB	1.37	2.69	2.77	−0.17	0.17	−0.44	S	29
MCQCISD-MPW	1.25	2.56	2.53	−0.33	0.33	−0.56	S	29
MCQCISD-TS	1.25	2.49	2.46	−0.38	0.38	−0.56	S	29
MCUT-MPWB	0.83	2.29	2.16	−0.68	0.68	−0.98	S	22
MCUT-TS	0.76	2.11	1.87	−0.86	0.86	−1.05	S	22
MCUT-MPW	0.62	2.07	1.77	−0.96	0.96	−1.19	S	22
MC−UT/3	2.79	3.71	4.30	1.16	1.16	1.52	PD	16
MC-QCISD/3	3.02	3.79	4.57	1.35	1.35	1.79	PD	23
CCSD/aug-cc-pVDZ	2.71	4.70	4.26	1.45	1.45	1.96	T	152

[a] See the footnotes of Table 1 for the description of S, T, PD, MSE, MUE, and cost. [b] Error = calculation − best estimate. [c] This is the dimer that gives the maximum error.

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 performance for the benzene dimer of MCG3-TS, MCG3-MPWB, and MCG3-MPW is similar (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. The fact that all three doubly hybrid MCG3 methods perform well supports the robustness of the approach. Note that the work by Sinnokrot and Sherrill[15,24] supports the conclusion that it is important to extrapolate to the complete-basis limit at the MP2 level or better because benzene dimers are unbound in some important geometries at the Hartree−Fock complete-basis limit. This requirement does not explain why the three MCG3-DFT methods outperform the other multilevel methods (G3SX, G3SX(MP3), CBS-QB3, MCG3/3) for benzene dimers, because all of these methods include a progression from small to large basis sets at the MP2 level. We believe that the empirical mixing of WFT and DFT methods is the key reason the present method obtain a balanced description of the benzene dimer interactions at a low cost.

Table 2 shows that the three N^6 multicoefficient extrapolated methods based on MC-QCISD/3,[45] namely MCQCISD-TS, MCQCISD-MPWB, and MCQCISD-MPW, outperform the three N^6 multicoefficient extrapolated methods based on MC-UT/3,[45] 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 1.5 orders of magnitude less expensive than the G3SX method. 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 N^6 multilevel 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,[33] but for benzene dimer interactions MCQCISD-MPWB is better. This is consistent with our previous finding that mPW[38] exchange and B95[40] correlation is a good combination of DFT functionals for nonbonded interactions,[51,52] for example, MPW1B95[51] and MPWB1K[51] outperform TPSS1KCIS[33] and mPW1PW91[38] 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,[33] 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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