Modeling Systems with $\pi-\pi$ Interactions Using the Hartree–Fock Method with an Empirical Dispersion Correction

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Modeling Systems with $\pi-\pi$ Interactions Using the Hartree–Fock Method with an Empirical Dispersion Correction

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ABSTRACT: The accuracy of the Hartree–Fock method with an empirical dispersion correction, HF-D3, to model interaction energies and locate constrained minimum geometries is tested against more conventional correlation methods, such as second-order perturbation theory and coupled cluster theory, and against the sophisticated effective fragment potential model. HF-D3 was applied to substituted-benzene dimers in both sandwich and T-shaped configurations and to DNA base pair complexes in both hydrogen bonded and stacked geometries. Overall, HF-D3 is found to be a plausible and cost efficient substitute for higher levels of electronic structure theory, such as MP2, in systems with $\pi-\pi$ interactions.

INTRODUCTION

Many important noncovalent interactions in bimolecular systems are a result of van der Waals (dispersion) interactions that arise from electron correlation. For example, the $\pi-\pi$ interactions of base pairs in the stacked structure of DNA and the processes of bimolecular recognition are largely due to weak dispersive interactions.\textsuperscript{1–5} Such processes are difficult to model due to the weakness of the interaction and shallowness of the potential energy surfaces.\textsuperscript{4,5} An example is the benzene dimer, which has a binding energy of 2–3 kcal/mol in the gas phase.\textsuperscript{6,7} High levels of electronic structure theory are generally required to accurately describe dispersion,\textsuperscript{6} but at a high computational cost. For instance, second-order Møller–Plesset perturbation theory (MP2)\textsuperscript{8} and coupled cluster (CC) theory,\textsuperscript{9} scale as $O(\eta^3)$ and $O(\eta^4)$, respectively, where $\eta$ represents the number of basis functions used in the system. Low levels of electronic structure theory, such as Hartree–Fock (HF) and most density functionals (DFs) in density functional theory (DFT) do not capture dispersion effects due to their use of the mean field approximation (independent particle model) but have a lower computational cost, scaling as $O(\eta^2)$–$O(\eta^4)$.

One solution to this problem of accuracy versus scaling is to add an empirical (D) dispersion correction to the energy obtained with a mean field level of theory (MT):

$$E_{MT-D} = E_{MT} - E_{disp}$$ (1)

Such an empirical correction to the HF energy was first proposed by Hepburn, Scoles, and Penco in 1975.\textsuperscript{10} Since 1975, there have been many attempts to accurately approximate dispersion onto MTs.\textsuperscript{11–18} A general form for the dispersion interaction energy from perturbation theory is\textsuperscript{11,14,19}

$$E_{disp} = \sum_{AB} \sum_{n=6/7/8...} C_{AB}^n \frac{f_n(r_{AB})}{r_{AB}^n}$$ (2)

Practical applications of eq 2 differ by their choice of damping functions $f_n(r_{AB})$, dispersion coefficients ($C_{AB}^n$), and the order ($n$) at which the series is truncated. The series is often truncated at $n \leq 10$ and often does not include the odd orders ($n = 7, 9$) as they average to zero in freely rotating species. The term $r_{AB}$ in eq 2 is the internuclear distance between atoms A and B.

Grimme and co-workers proposed a successful series of empirical atom pairwise dispersion corrections for DFT functionals, denoted -D1, -D2, and -D3.\textsuperscript{20–22} DFT-D1,2 are both variants of an atom pairwise sum over $C_{AB}/R^6$ potentials.\textsuperscript{20,21} DFT-D3 differs from its predecessors by allowing the addition of higher order even terms ($n \geq 8$), as well as a three-body contribution to the dispersion energy. In addition, the dispersion coefficients ($C_{AB}^n$) and cutoff radii for the damping function in DFT-D3 are computed from first principles. Fractional coordination numbers are utilized to interpolate the $C_{AB}$ values. This method is believed to improve the accuracy of $C_{AB}$ since it allows atoms to account for their chemical environment. Another feature of -D3 is the adjustment of only two global parameters. In practice, -D3 is usually truncated at the order $n = 8$ and the three-body term is not used as it overestimates the energy contribution of the three-body dispersion interactions in tested systems.\textsuperscript{22}

Sure and Grimme recently published an implementation of -D3 applied to HF using small basis sets, denoted HF-3C.\textsuperscript{23} By applying an empirical dispersion correction to HF instead of DFT, intrinsic double counting of electron correlation and possible dependence on error cancelation are avoided, as DFT does intrinsically account for some short-range electron
correlation, whereas HF includes no electron correlation aside from the Fermi hole. Some DFs do incorporate longer-range electron correlation effects (e.g., the M06 suite by Zhao and Truhlar\textsuperscript{24–26}), such as dispersion. In HF-3C, two additional corrections are used with the -D3 method. The first corrects for the basis set superposition error (BSSE), and the second is a short-range correction for basis set deficiencies. Both of these corrections are required to maintain the accuracy of the method due to the use of a small basis set. The incorporation of these corrections includes additional parameters.\textsuperscript{23}

In the present investigation, the -D3 method is applied to HF, denoted HF-D3, without the two aforementioned additional corrections, with a large Pople basis set. HF-D3 has been used before in various applications of electronic structure theory\textsuperscript{27–30} and has been benchmarked using small or minimal basis sets.\textsuperscript{31} In this work, HF-D3 is applied to systems with $\pi - \pi$ interactions and the resulting interaction energies are compared to conventional correlation method calculations, such as MP$^2$\textsuperscript{32} and coupled cluster with singles, doubles, and perturbative triples CCSD(T),\textsuperscript{33} and the general effective fragment potential (EFP) method.\textsuperscript{34,35}

### COMPUTATIONAL METHODS

HF-D3 was implemented using the General Atomic and Molecular Electronic Structure System (GAMESS)\textsuperscript{34,35} software package. HF-D3 calculations were performed with the 6-311+G(d,p) basis set. The expressions for the -D3 dispersion correction\textsuperscript{22} (eq 3) and the damping function\textsuperscript{36} (eq 4) used are

$$E_{\text{disp}} = \sum_{AB} \sum_{n} s_{n} \frac{c_{nAB}}{r_{AB}^{6}} - \sum_{AB} \frac{1}{1 + 6(r_{AB} / (s_{n} r_{0}^{AB}))^{3}}$$

Equation 4 is often referred to as the zero-damping scheme. Another damping scheme, recommended by Grimme et al.,\textsuperscript{37} is the Becke and Johnson damping\textsuperscript{38,39} (not currently available in GAMESS), which appears to improve the mean absolute deviation of HF-D3 from benchmarked data on the S22 test set.\textsuperscript{31} In the present work, the scaling factors $s_{6}$ and $s_{8}$ were set equal to unity and the “steepness” parameters, $\alpha_{6}$ and $\alpha_{8}$, were set to 14 and 16, respectively, to reduce the error in the dispersion correction for typical covalent bond distances, as prescribed by Grimme et al.\textsuperscript{32} The two global parameters, $s_{6}$ and $s_{8}$, were determined by Grimme to be 1.158 and 1.746, respectively, for the HF-D3 method by a standard least-squares error fitting procedure. Note that the values of the global parameters for HF-D3 were not reported in ref 22 but were included in the 2010 public release of the Grimme -D3 code (dftd3.1.2), which was incorporated into GAMESS. Interaction energies ($E_{\text{int}}$) are taken to be the difference between the total energy ($E_{\text{Total}}$) of a system and the sum of the monomer energies ($E_{k}$).

$$E_{\text{int}} = E_{\text{Total}} - \sum_{k} E_{k}$$

**Substituted Benzene Dimers.** The HF-D3 method was applied to benzene and substituted benzene dimers (BD) in the sandwich, T-shaped(1), and T-shaped(2) configurations using the MP2/aug-cc-pVTZ optimized rigid monomers, as described by Sinnokrot and Sherrill\textsuperscript{3} (Figure 1). The substituted species are phenol, toluene, fluorobenzene, and benzonitrile. The C–C and C–H bond lengths for benzene are 1.3942 and 1.0822 Å, respectively. Phenol was restricted to C$_{s}$ symmetry so that the hydrogen atom on the alcohol group remains in the plane of the ring. Toluene was also restricted to C$_{s}$ symmetry so that one hydrogen atom in the methyl group is above the plane of the ring and the other two hydrogen atoms are below the plane of the ring. Intermonomer distances (R), defined as the distance between the ring centers, were optimized to within 0.05 Å precision. The interaction energies were calculated and compared to the estimated CCSD(T)/aug-cc-pVTZ, MP2/aug-cc-pVDZ (MP2/accd), and MP2/aug-cc-pVTZ (MP2/acct) data of ref 5 and to the corresponding EFP interaction energies.\textsuperscript{4} Effective fragment potentials (EFPs) are intermolecular interaction potentials that are generated from first-principles quantum mechanics with no empirically fitted parameters.\textsuperscript{32,33} EFPs have been shown by Flick et al.\textsuperscript{50} to predict intermolecular interaction energies to an accuracy that is comparable to that of MP2 for a wide variety of interaction types, ranging from hydrogen bonding to van der Waals interactions.

The CCSD(T) interaction energies were estimated in ref 5 by assuming that improvements to basis set and level of theory are additive. The same procedure has been used successfully in many composite methods [e.g., the Pople G3,\textsuperscript{41} W4,\textsuperscript{42} and ccCA-CC(2,3)\textsuperscript{43} composite methods]. The interaction energies in ref 5 were also corrected for possible basis set superposition error (BSSE) via the counterpoise-correction of Boys and Bernardi.\textsuperscript{44} In the present work, the dispersion contribution to the HF-D3 interaction energy is also compared to the symmetry adapted perturbation theory (SAPT)\textsuperscript{45} data of ref 5 and the EFP results of ref 4.

**DNA Base Pairs.** The HF-D3 method was also applied to (Watson–Crick) hydrogen bonded (_wc) and stacked (_s and _s1) DNA base pairs. The geometries used for these calculations were the resolution of the identity (RI)-MP2 equilibrium geometries of guanine-cytosine (G–C _wc and G–C _s, respectively) and adenine-thymine (A–T _wc and A–T _s1 respectively), taken from the JSCH-2005 benchmark set provided by Jurečka et al.\textsuperscript{3} [See Figure 2 for the notations used here.] Interaction energies were calculated and compared to the MP2 and estimated CCSD(T) interaction energies from ref 3 and to the EFP interaction energies reported by Smith and Gordon.\textsuperscript{46} The A–T _wc and A–T _s1 interaction energies are compared to the CCSD(T) results from Takantani et al.\textsuperscript{47} The estimated CCSD(T) energies used in ref 3 were counterpoise-corrected for BSSE, and the energies were extrapolated to the complete basis set (CBS) limit by a two-point extrapolation scheme.\textsuperscript{48}
Interaction energy curves (IECs) were calculated by varying the relative positions of the two monomers starting from the RI-MP2 equilibrium geometries, keeping the internal geometries of each monomer rigid. Four types of IECs were calculated: translation, rotation, parallel tilt, and mirrored tilt (Figure 2). Translation IECs were calculated by varying the distance \( R \) between the centers of mass of each monomer at 0.05 Å increments through the minima and 0.50 Å increments at larger distances. Rotation IECs were calculated by rotating (by an angle \( \Phi \)) a single (rigid) monomer about the axis formed by the centers of mass, mostly at 10° intervals, with 1° intervals near the RI-MP2 minima. Tilting IECs were calculated by tilting both monomers by the same degree of tilt (\( \alpha \) or \( \beta \)) at the angle \( \theta \). \( \theta \) is a projected angle on the planes that are perpendicular to the centers of mass axis at each respective center of mass. Atoms are colored white hydrogen, black carbon, blue nitrogen, and red oxygen.

![Figure 2. DNA base pair geometries: hydrogen bonded and stacked adenine-thymine \([A\cdots T\text{\_wc} (A) \text{ and } A\cdots T\text{\_s1 (C)}, \text{ respectively}]\) and guanine-cytosine \([G\cdots C\text{\_wc} (B) \text{ and } G\cdots C\text{\_s (D), respectively}]\) base pair structures. RI-MP2 equilibrium geometries are from the JSCH-2005 benchmark set of ref 3. \( R \) is the distance between the centers of mass. \( \Phi \) is the monomer degree of rotation about the axis formed by the centers of mass. \( \alpha \) and \( \beta \) are degrees for parallel and mirrored tilt, respectively, at the angle \( \theta \). \( \theta \) is a projected angle on the planes that are perpendicular to the centers of mass axis.

Table 1. Projected Angles of DNA Base Pairs at RI-MP2 Equilibrium Geometries

<table>
<thead>
<tr>
<th>Base Pair</th>
<th>( \theta_1 )</th>
<th>( \theta_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>G\cdots C_wc</td>
<td>174.57°</td>
<td>3.82°</td>
</tr>
<tr>
<td>G\cdots C_s</td>
<td>354.10°</td>
<td>135.91°</td>
</tr>
<tr>
<td>A\cdots T_wc</td>
<td>0.95°</td>
<td>357.84°</td>
</tr>
<tr>
<td>A\cdots T_s1</td>
<td>101.29°</td>
<td>234.84°</td>
</tr>
</tbody>
</table>

“Projected angles for the methyl carbon atom of thymine and amine nitrogen atom of adenine are given by \( \theta_1 \) and \( \theta_2 \), respectively. Projected angles for the amine nitrogen atoms of guanine and cytosine are given by \( \theta_1 \) and \( \theta_2 \), respectively.”

RESULTS AND DISCUSSION

Sandwich Substituted Benzene Dimers. Table 2 reports HF-D3 interaction energies at optimized distances \( R \) with the corresponding MP2/accd, MP2/acct, and estimated CCSD(T) results of ref 5 and EFP results of ref 4. HF-D3 consistently overestimates (more positive) the optimized distances for all BD systems, including T-shaped(1) and T-shaped(2) configurations, by 0.05−0.15 Å, with a mean deviation of 0.11 Å for the sandwich BD configurations relative to the estimated CCSD(T) minima. For comparison, EFP has a mean deviation of 0.08 Å for the optimized sandwich BD, while MP2/accd and MP2/acct both underestimate (less positive) the optimized distances with a mean deviation of \(-0.04 \text{ and } -0.13 \) Å, respectively. The HF-D3 interaction energies at optimized sandwich BD minima are surprisingly accurate with a maximum absolute deviation of 0.30 kcal/mol for benzene−benzene, a minimum deviation of \(-0.04 \text{ kcal/mol for fluorobenzene−}

benzene, and an average deviation of 0.07 kcal/mol, all with respect to estimated CCSD(T). Therefore, HF-D3 interaction energies at the optimized sandwich BD geometries are more accurate than MP2/accd, MP2/acct, and EFP, which have

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maximum absolute deviations of 1.44, 1.81, and 0.86 kcal/mol and average deviations of −1.26, −1.61, −0.60 kcal/mol, respectively. The HF-D3 interaction energies are in good agreement with those predicted by estimated CCSD(T), with deviations that are less than 0.3 kcal/mol. Both HF-D3 and estimated CCSD(T) predict that all interaction energies of substituted benzene–benzene dimers are lower (more negative) than that of the unsubstituted benzene–benzene dimer.

**T-shaped(1) Substituted Benzenes Dimer.** For the T-shaped(1) BD, HF-D3 overestimates (more positive) the optimized R distances with a maximum deviation of 0.15 Å for benzonitrile–benzene, a minimum deviation of 0.05 Å for fluorobenzene–benzene and a mean deviation of 0.10 Å, with respect to the estimated CCSD(T) values (Table 2). Comparatively, EFP and MP2/acct have mean deviations of 0.18 and −0.10 Å, respectively. The intermolecular distances obtained with the MP2/accd method show the best agreement with CCSD(T), with a maximum absolute deviation of 0.05 Å for fluorobenzene–benzene and a mean deviation of −0.01 Å. For the T-shaped(1) structure, the interaction energies are closest to the estimated CCSD(T) energies for benzene–benzene, and a mean deviation of 0.07 kcal/mol. HF-D3 agrees with the estimated CCSD(T) interaction energies in the sense that the optimized T-shaped(1) BD interaction energies are lower (more negative) than the corresponding optimized sandwich BD interaction energies.

**T-shaped(2) Substituted Benzenes Dimer.** For the T-shaped(2) BD, HF-D3 again overestimates (more positive) the optimized R distances with a maximum deviation of 0.11 Å for benzonitrile–benzene, a minimum deviation of 0.05 Å for toluene–benzene, and a mean deviation of 0.08 Å, with respect to the estimated CCSD(T) method (Table 2). In comparison, the mean deviations obtained with EFP and MP2/acct are 0.16 and −0.12 Å, respectively. T-shaped(2) MP2/accd optimized R distances are the most accurate compared to the estimated CCSD(T) distances, with a maximum absolute deviation of 0.10 Å for toluene–benzene and a mean deviation of −0.03 Å. For the T-shaped(2) BD HF-D3 interaction energies are not as accurate as HF-D3 sandwich BD interaction energies. The HF-D3 method consistently overestimates (more negative) the T-shaped(2) interaction energies with a maximum deviation of −0.80 kcal/mol for toluene-benzene, a minimum deviation of −0.71 kcal/mol for benzene-benzene, and a mean deviation of −0.75 kcal/mol, with respect to the estimated CCSD(T) interaction energies. Compared to MP2/acct and MP2/accd with mean deviations of −0.86 and −0.57 kcal/mol, respectively, for the predicted interaction energies, HF-D3 interaction energies provide an accuracy that is comparable to that of MP2. T-shaped(2) BD EFP interaction energies are the

### Table 2. Interaction Energies ($E_{int}$) for the Sandwich, T-Shaped(1), and T-Shaped(2) Configurations of Substituted Benzene Dimers at Optimized Intermonomer Distances ($R$)

<table>
<thead>
<tr>
<th>X</th>
<th>method</th>
<th>sandwich</th>
<th>T-shaped(1)</th>
<th>T-shaped(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R$ (Å) $E_{int}$ (kcal/mol)</td>
<td>$R$ (Å) $E_{int}$ (kcal/mol)</td>
<td>$R$ (Å) $E_{int}$ (kcal/mol)</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>est. CCSD(T)/aug-cc-pVTZ$^a$</td>
<td>3.90</td>
<td>−1.80</td>
<td>4.99</td>
</tr>
<tr>
<td></td>
<td>MP2/aug-cc-pVDZ$^a$</td>
<td>3.80</td>
<td>−2.90</td>
<td>5.01</td>
</tr>
<tr>
<td></td>
<td>MP2/aug-cc-pVTZ$^a$</td>
<td>3.70</td>
<td>−3.26</td>
<td>4.89</td>
</tr>
<tr>
<td></td>
<td>EFP$^b$</td>
<td>3.95</td>
<td>−2.17</td>
<td>5.15</td>
</tr>
<tr>
<td></td>
<td>HF-D3/6-311G+(dp)</td>
<td>4.00</td>
<td>−1.50</td>
<td>5.10</td>
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<tr>
<td>OH</td>
<td>est. CCSD(T)/aug-cc-pVTZ$^a$</td>
<td>3.80</td>
<td>−2.17</td>
<td>5.00</td>
</tr>
<tr>
<td></td>
<td>MP2/aug-cc-pVDZ$^a$</td>
<td>3.70</td>
<td>−3.40</td>
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<td>3.60</td>
<td>−3.75</td>
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<td></td>
<td>EFP$^b$</td>
<td>3.90</td>
<td>−2.72</td>
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<td>EFP$^b$</td>
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<td>HF-D3/6-311G+(dp)</td>
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<tr>
<td>F</td>
<td>est. CCSD(T)/aug-cc-pVTZ$^a$</td>
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<td>−3.50</td>
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<td>−3.81</td>
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<td>EFP$^b$</td>
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<tr>
<td>CN</td>
<td>est. CCSD(T)/aug-cc-pVTZ$^a$</td>
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<td>−3.05</td>
<td>4.90</td>
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<td>4.90</td>
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<td>MP2/aug-cc-pVTZ$^a$</td>
<td>3.60</td>
<td>−4.86</td>
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<td></td>
<td>EFP$^b$</td>
<td>3.85</td>
<td>−3.91</td>
<td>5.15</td>
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<tr>
<td></td>
<td>HF-D3/6-311G+(dp)</td>
<td>3.85</td>
<td>−3.30</td>
<td>5.05</td>
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</tbody>
</table>

$^a$MP2 and estimated CCSD(T) results taken from ref 5. $^b$EFP results taken from ref 4.
close to the estimated CCSD(T) values, with a maximum absolute deviation of 0.22 kcal/mol for benzene—benzene and a mean deviation of 0.09 kcal/mol. HF-D3 agrees with the estimated CCSD(T) method in that the optimized T-shaped(2) BD interaction energies are lower (more negative) than their corresponding optimized sandwich BD geometries, except for benzonitrile-benzene. For benzonitrile—benzene, HF-D3 and estimated CCSD(T) agree that the interaction energy of the sandwich configuration is lower than that of the T-shaped(2) configuration.

Dispersion Component of Interaction Energies. HF-D3, SAPT, and EFP dispersion contributions to the total interaction energy are presented in Table 3. The geometries in Table 3 correspond to an intermonomer distance of 3.70 Å for the sandwich BD geometries and 4.90 Å for the T-shaped(1) and T-shaped(2) BD geometries. The HF-D3 dispersion interaction energies for the sandwich BD structures are consistently slightly smaller in magnitude than those predicted by SAPT, with an average deviation of 0.64 kcal/mol. The EFP dispersion interaction energies have an average deviation of 0.16 kcal/mol relative to SAPT. The HF-D3 dispersion interaction energies for the T-shaped(1) BD species are smaller in magnitude than the corresponding SAPT values, with an average deviation of 0.12 kcal/mol. EFP has an average deviation of 0.38 kcal/mol relative to SAPT. The HF-D3 and EFP deviations from the SAPT dispersion interaction energies for the T-shaped(2) BD species are similarly small, less than 0.5 kcal/mol. So, both HF-D3 and EFP give an excellent accounting of the dispersion interaction energies for benzene dimers.

DNA Base Pair Interaction Energies. Total interaction energies for the DNA base pair systems at the RI-MP2 optimized geometries for several levels of theory are reported in Table 4. The previous EFP calculations did not include the charge transfer interaction and are denoted EFP*. HF-D3 reproduces the estimated CCSD(T) interaction energies for the base pairs very well, with the largest deviation being 2.4 kcal/mol. This performance is generally better than that of both MP2 and RI-MP2, not quite as good as EFP and slightly better than EFP*. It is also noteworthy that the agreement of EFP with estimated CCSD(T) is better when the charge transfer interaction is included.

Interaction Energy Curves. Some HF-D3/6-311+G(d,p), EFP, and MP2/6-311+G(d,p) interaction energy curves for the DNA base pair systems are presented in Figures 3–6. The G···C_wc HF-D3 and EFP IECs (Figure 3) both closely follow the MP2 interaction energy curves. The HF-D3 G···C_wc IECs tend to be slightly lower (more negative) than the MP2 IECs near minima, but still within 1–2 kcal/mol of the MP2 interaction energies. The HF-D3 G···C_wc IECs become higher (more positive) than both the MP2 IECs as the curves move away from the minima, except for the case of the translation IECs. For the G···C_wc translation IECs, HF-D3, and MP2 interaction energies both asymptotically approach zero. The A···T_wc IECs (Figure 5) follow similar trends as the G···C_wc IECs. The HF-D3 curves closely follow the MP2 A···T_wc IECs to within 1 kcal/mol near the energy minima.

For G···C_s the MP2 IECs are significantly lower (more negative) than both the HF-D3 and EFP IECs. This is due to the tendency of MP2 to over bind the stacked geometry, especially for larger basis sets. This over binding is seen at the stacked RI-MP2 minima in Table 4: The MP2/6-311+G(d,p) interaction energy is 5.5 and 6.9 kcal/mol lower than the estimated CCSD(T) values for G···C_s and A···T_s1, respectively. MP2 also over binds the interaction energies of the sandwich BD in ref 5 (Table 2). This overbinding of MP2 interaction energies also occurs in the A···T_s1 EICs (Figure 6). The HF-D3 A···T_s1 IECs are closer to the EFP IECs and are more accurate than MP2 at the RI-MP2 minimum relative to estimated CCSD(T).

Table 3. Dispersion Energy Contributions (kcal/mol) at Fixed Intermonomer Distances (R) for Sandwich, T-Shaped(1), and T-shaped(2) Substituted Benzene Dimer Structures

<table>
<thead>
<tr>
<th>X</th>
<th>SAPT</th>
<th>EFP</th>
<th>HF-D3</th>
<th>SAPT</th>
<th>EFP</th>
<th>HF-D3</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>−5.53</td>
<td>−6.38</td>
<td>−5.88</td>
<td>−4.37</td>
<td>−3.83</td>
<td>−4.22</td>
</tr>
<tr>
<td>OH</td>
<td>−6.72</td>
<td>−6.55</td>
<td>−6.11</td>
<td>−4.37</td>
<td>−4.07</td>
<td>−4.22</td>
</tr>
<tr>
<td>CH₃</td>
<td>−7.39</td>
<td>−7.03</td>
<td>−6.46</td>
<td>−4.46</td>
<td>−4.16</td>
<td>−4.24</td>
</tr>
<tr>
<td>F</td>
<td>−6.49</td>
<td>−6.31</td>
<td>−5.93</td>
<td>−4.22</td>
<td>−3.92</td>
<td>−4.20</td>
</tr>
<tr>
<td>CN</td>
<td>−7.01</td>
<td>−6.87</td>
<td>−6.38</td>
<td>−4.29</td>
<td>−3.83</td>
<td>−4.22</td>
</tr>
</tbody>
</table>

*Intermonomer distances are 3.70 Å for sandwich geometries. †Intermonomer distances are 4.90 Å for T-shaped geometries. ‡SAPT results taken from ref 5. §EFP results taken from ref 4.

Table 4. Interaction Energies of DNA Base Pair Complexes at Optimized RI-MP2 Geometries

<table>
<thead>
<tr>
<th>method</th>
<th>G···C_wc</th>
<th>G···C_s</th>
<th>A···T_wc</th>
<th>A···T_s1</th>
</tr>
</thead>
<tbody>
<tr>
<td>RI-MP2/aug-cc-pVDZ</td>
<td>−28.7</td>
<td>−18.5</td>
<td>−14.8</td>
<td>−13.1</td>
</tr>
<tr>
<td>RI-MP2/aug-cc-pVTZ</td>
<td>−30.4</td>
<td>−20.0</td>
<td>−16.1</td>
<td>−14.4</td>
</tr>
<tr>
<td>RI-MP2/aug-cc-pVQZ</td>
<td>−31.1</td>
<td>−20.5</td>
<td>−16.5</td>
<td>−14.8</td>
</tr>
<tr>
<td>EFP</td>
<td>−30.4</td>
<td>−20.6</td>
<td>−14.0</td>
<td>−10.7</td>
</tr>
<tr>
<td>EFP*</td>
<td>−33.7</td>
<td>−21.7</td>
<td>−16.2</td>
<td>−11.5</td>
</tr>
<tr>
<td>MP2/6-311+G(dp)</td>
<td>−30.6</td>
<td>−24.5</td>
<td>−16.4</td>
<td>−18.6</td>
</tr>
<tr>
<td>HF-D3/6-311+G(dp)</td>
<td>−32.1</td>
<td>−21.4</td>
<td>−16.2</td>
<td>−13.3</td>
</tr>
<tr>
<td>est. CCSD(T)</td>
<td>−32.1</td>
<td>−19.0</td>
<td>−16.7</td>
<td>−17.7</td>
</tr>
</tbody>
</table>

*Energies are in kcal/mol. †CBS estimated CCSD(T) energies, RI-MP2 energies, and optimized base pair geometries taken from ref 3. ‡Except for A···T_wc and A···T_s1, CBS CCSD(T) data were taken from ref 47. §EFP* energies taken from ref 46. EFP energies include charge transfer terms that are included in ref 46.

Do not hallucinate.
Figure 3. G···C_{wc} interaction energy curves.

Figure 4. G···C_{s} interaction energy curves.
Figure 5. $A \cdots T_{\text{wc}}$ interaction energy curves.

Figure 6. $A \cdots T_{\text{s1}}$ interaction energy curves.
including the estimated CCSD(T) benchmarks. For benzene dimers (BD), HF-D3 calculated minimum energy geometries along constrained optimizations are within 0.05–0.15 Å of the estimated CCSD(T) benchmark minima, comparable in accuracy to EFP and MP2. The HF-D3 BD interaction energies at the optimized minima are within 0.04–0.91 kcal/mol of the estimated CCSD(T) benchmark minimum energies. The ability of HF-D3 to accurately model interaction energies is comparable to that of EFP and MP2 in systems with relatively small dispersion contributions to the interaction energy, such as the hydrogen-bonded base pairs and T-shaped BD systems tested in this investigation. The accuracy of HF-D3 for interaction energies is comparable to that of EFP and better than MP2 for systems with large dispersion contributions, such as π−π stacking complexes, in which MP2 is known to overbind.5

The findings in the present work are consistent with those found by Pruitt et al.,29 who found that the HF-D3 method is able to reproduce relative energies with an accuracy comparable to MP2 on argon and water clusters. It was noted that HF-D3 performed better for systems for which short to medium range correlation effects are less important, such as argon clusters and benzene dimer.29

For the systems tested in the present work, the HF-D3 dispersion contribution to the interaction energy is comparable in accuracy to both SAPT and EFP. It is concluded that the HF-D3 model is a reasonable choice for calculating interaction energies of chemical systems with π−π interactions near local energy minima and is a plausible, cost efficient replacement for MP2 for such systems.

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Notes
The authors declare no competing financial interest.

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