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The effect of electron correlation in intermolecular interactions can be electrostatically dominated

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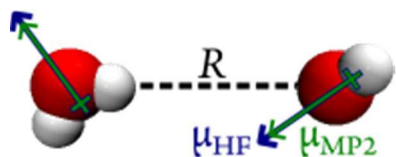
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ABSTRACT

The electron-electron correlation energy is negative, and attractive dispersion interactions are entirely a correlation effect, so the contribution of correlation to intermolecular binding is commonly assumed to be negative, or binding in nature. However, there are many cases where the long-range correlation binding energy is positive with certain geometries of the water dimer as a prominent example. Geometries with dipoles misaligned can also have an electrostatically dominated, though negative, long-range correlation binding. In either case, the interaction decays as R^{-3} . This has its origin in the systematic overestimation of dipole moments by Hartree–Fock theory, leading to a reduction in the calculated electrostatic attraction upon inclusion of correlation. Thus, energy decomposition analyses that include correlation but do not correct mean field electrostatic terms are sub-optimal. Attenuated second-order Møller–Plesset theory, which smoothly truncates long-range electron correlation effects to zero, can, paradoxically, have the correct long-range behavior for many intermolecular interactions.

TOC GRAPHICS

$$\lim_{R \rightarrow \infty} \Delta E^{(2)}(\text{H}_2\text{O}-\text{H}_2\text{O}) \propto R^{-3}$$

1
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3 **KEYWORDS** intermolecular interactions, ab initio calculations, electron correlation, water
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6 dimer, energy decomposition analysis.
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Ab initio wave function methods that include treatment of electron correlations are widely used for the accurate calculation of intermolecular interactions (*e.g.* for a bimolecular AB complex), using the supermolecule approach in which $\Delta E = E(AB) - E(A) - E(B)$. Correlation methods correct the mean field Hartree–Fock (HF) approximation for the effect of instantaneous electron–electron correlations: $E = E_{HF} + E_{corr}$. Common examples include high accuracy coupled cluster theory with singles, doubles, and perturbative triples (CCSD(T))¹, and, for larger molecules, the more computationally efficient second order Møller–Plesset perturbation theory (MP2)².

The contribution of electron correlation, E_{corr} , to absolute molecular energies, E , is negative semi-definite and crucial for calculating accurate intermolecular interactions, though it is typically only about 1% of the total energy. CCSD(T) in particular^{3,4,5} — and sometimes even MP2 theory (*e.g.* for hydrogen-bonded systems^{6,7}) — is more accurate than most widely used density functionals for intermolecular interactions^{8,9}, despite continuing progress in functional development. With sufficiently large basis sets, both CCSD(T) and MP2 are tremendously successful, although MP2 is known to significantly overestimate the strength of stacking interactions^{10,11,12}, and the high cost of CCSD(T) prevents application to large molecules without additional approximations. Accordingly, modifications are sought to MP2 theory to improve its accuracy for intermolecular interactions without increasing cost, such as spin-component scaling^{13,14,15} and electronic attenuation^{16,17}.

Physically, the HF reference captures some key aspects of intermolecular interactions, such as permanent electrostatics (either attractive or repulsive) and Pauli repulsion associated with the frozen orbitals of isolated fragments, and the induced orbital interactions or mixings. To unravel these contributions, energy decomposition analysis (EDA) methods, such as the Kitaura–

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3 Morokuma method¹⁸ and its many descendants^{19,20,21,22,23}, partition the HF binding energy, ΔE_{HF}
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6 , into physically motivated components: $\Delta E_{HF} = \Delta E_{FRZ} + \Delta E_{IND}$. Some EDAs further partition the
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8 induced orbital interactions into terms associated with polarization (on a fragment) and donor–
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10 acceptor orbital interactions (between fragments)^{24,25,26,27}.

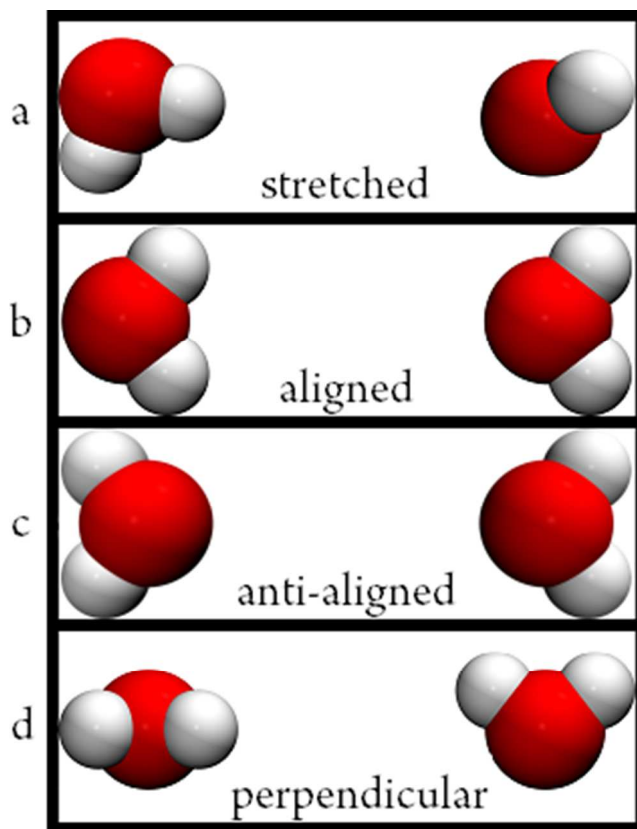
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13 How should an EDA be modified when electron correlation is included in the calculation?
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15 Inclusion of correlation accounts for purely attractive dispersion forces between molecules due to
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17 correlation in the temporary multipoles created by electron movements, an effect entirely absent
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19 in the HF reference. For neutral, non-polar molecules, dispersion is usually the most important
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21 long-range interaction, decaying as the inverse of the sixth power of the separation between
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23 molecules. Given that dispersion interactions are purely attractive, and the correlation energy
24
25 itself is negative semi-definite, the simplest modification to such EDAs is to include the
26
27 correlation binding energy (CBE) as an additional term^{21,23}, labeled as dispersive: $\Delta E_{DISP} = \Delta E_{corr}$
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30 There have been some additional attempts^{28,29} to further partition the correlation energy into a
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32 purely dispersive part, where there is no net transfer of electrons, a charge-transferring
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34 contribution, and intra-fragment correlation.
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40 This letter will present some calculations which challenge the identification of ΔE_{corr} as
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42 dispersive by illustrating that for many intermolecular interactions, the long-range contribution
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44 of the correlation energy is, in fact, electrostatically dominated and can either be binding or anti-
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46 binding: $\Delta E_{corr} > 0$. This result appears surprising since it is intuitive that a supermolecule
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48 should have more correlation than the isolated sum of its parts. Thus one expects that the CBE
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50 should be negative semi-definite, consistent with it being primarily dispersive. While that is of
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52 course true for non-overlapping atoms, real systems often differ from this idealization in
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54 important ways. It can only be accurate in general if, despite those differences, none of the other
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3 effects captured by post HF methods are ever as important as dispersion. Though this fact has
4 been previously described³⁰ in an analysis that was understood and mentioned in several papers
5 over the following few years^{31,32,33,34}, especially among the symmetry-adapted perturbation
6 theory community, it is not widely known in quantum chemistry (indeed we are grateful to a
7 referee for pointing out these references to us). Because of intrinsic interest, and significance for
8 EDAs, improvements to Hartree-Fock for dispersion, and the attenuation of MP2, it is useful and
9 timely to explore the nature of the long-range CBE in detail, and examine the resulting
10 implications.
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22 In investigating the types of effects the correlation energy can describe, the water dimer will be
23 used as an example system, though as we shall see, the results immediately generalize to many
24 other systems. All calculations were performed with Q-Chem 4.0.³⁵ There are four geometries of
25 interest. The first is the equilibrium geometry of the dimer where one molecule is rigidly
26 translated along the axis between the centers of mass of the two molecules, as depicted in Figure
27 1(a), which will be referred to as the stretched equilibrium geometry. Next is two aligned
28 coplanar water molecules with oxygen atoms separated along the axis parallel to the molecules'
29 dipoles, which is depicted in Figure 1(b) and will be referred to as the aligned geometry. This
30 geometry was chosen to maximize favorable electrostatic interactions. The next is similar to the
31 previous, but with one molecule flipped so the dipoles are antiparallel, and is depicted in Figure
32 1(c) and will be referred to as the anti-aligned geometry. This geometry was chosen to maximize
33 unfavorable electrostatic interactions. Last is the geometry with two water molecules arranged
34 with perpendicular dipoles with oxygen atoms separated along the axis perpendicular to both
35 molecules' dipoles, which is depicted in Figure 1(d), and will be referred to as the perpendicular
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3 geometry. This geometry was chosen to minimize electrostatic interactions, by making the
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6 dipole–dipole interaction zero.
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36 **Figure 1.** Four different geometries of the water dimer. The
37 stretched geometry is based on the S22 equilibrium geometry. The
38 other three geometries each have equivalent monomers with bond
39 length of 0.9584 Å and bond angle of 104.46°.
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46 The binding energy curves for the geometries with intermolecular separation beyond the
47 equilibrium distance are shown below in Figure 2. The calculations were done with resolution of
48 the identity approximation MP2 (RIMP2) in the aug-cc-pVQZ basis set and the corresponding
49 auxiliary basis set, without the frozen core approximation or counterpoise correction. There is
50 nothing particularly surprising in this graph. The perpendicular and anti-aligned geometries are
51 repulsive everywhere, though the perpendicular geometry has a local minimum in the short
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range. The stretched equilibrium geometry is lowest in energy in the short range, due to hydrogen bonding. And the aligned geometry is lowest in energy in the long range, where the dipole interaction is most important.

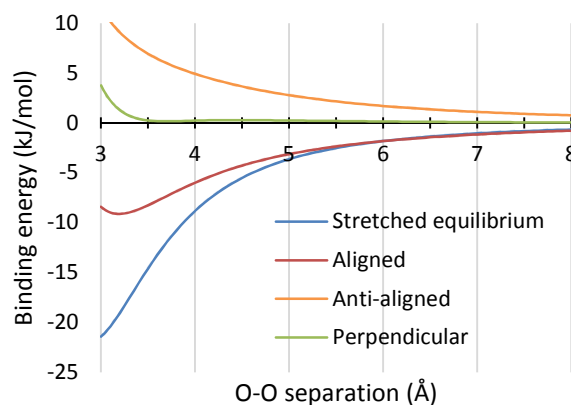
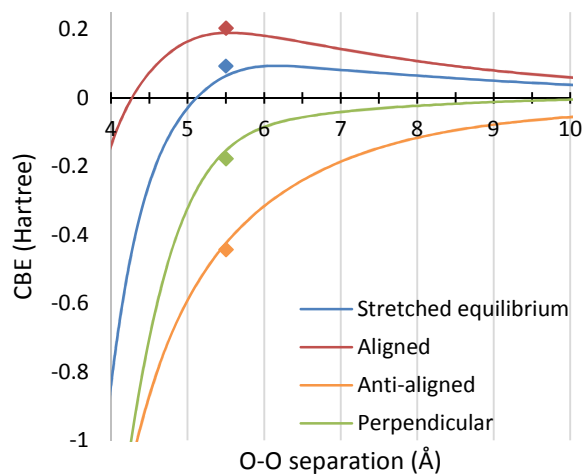


Figure 2. RIMP2 binding energy curves for the water dimer in four different geometries.

However, when focusing only on the correlation contribution to the binding energy, an unexpected effect is visible. As can be seen in Figure 3, for the stretched equilibrium and the aligned geometries, the CBE is positive beyond the equilibrium separation, meaning that MP2 binds the dimer less strongly than HF. The maximum value here is small, less than 0.2 kJ/mol, but still large enough to be noticeable. It defines the entire long range interaction of the dimers, all the way out to infinite separation. Furthermore, the CBE for the anti-aligned geometry decays much more slowly than the expected inverse sixth power of intermolecular separation. The positive CBE is not limited to MP2. The diamonds in Figure 3 are the CBE values calculated with CCSD(T), and show the same effect as in MP2. Neither is this result basis set dependent. Figure 4 shows the curve for the stretched equilibrium geometry in other basis sets. The magnitude of the maximum is somewhat larger with aug-cc-pVTZ, and slightly larger still with

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3 aug-cc-pVDZ. However, differences are small and the effect is definitely present in the smaller
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5 basis sets, and the trend implies that it will be present even at the basis set limit.
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Figure 3. RIMP2 correlation binding energy curves for the water dimer in four different geometries, along with a CCSD(T) value (the diamonds) at 5.5 Å for each.

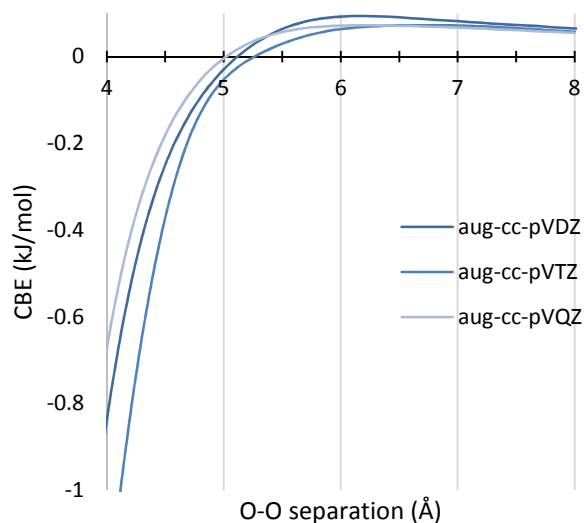


Figure 4. Correlation binding energy (CBE) curves for water dimer in the stretched equilibrium geometry, in three different basis sets. (The auxiliary basis set corresponds to the main basis set in each case.)

The positive CBE observed here contradicts our previously mentioned intuition that the treatment of electron correlation should always contribute to binding. EDAs that define dispersion as the CBE implicitly make this assumption since physical dispersion is a purely attractive force. A positive CBE is potentially noticeable to anyone who performs post HF binding energy calculations, and was discussed in the late 1980s^{30,31,32,33,34}. However, knowledge of positive CBE does not seem to be widespread in the general quantum chemistry community, and several recent methods do not properly account for its implications, as we shall see below. What, then, is the cause of the positive CBE? As has been shown, it is not related to the particular post HF method or basis used. Therefore, it would seem to be an actual effect rather than a computational artifact. The tails of the curves for the stretched equilibrium and aligned geometries both decay as the inverse of the cube of the separation between the molecules. Since

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3 this is the characteristic long range behavior of dipole–dipole interactions, it suggests that the
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5 explanation lies in the electrostatics.
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8 Hartree–Fock has a tendency to overestimate the strength of dipoles of molecules^{36,37,38,39}. This
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10 can be thought of as a result of the HF model being slightly too ionic in character due to neglect
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12 of correlation, or the fact that anti-bonding orbitals with opposite polarity to bonding orbitals
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14 acquire small occupation numbers when correlation is included. Thus, post HF methods calculate
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16 a smaller dipole as part of providing a more accurate description of the molecules. This
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18 difference can be seen in water. As shown in Table 1, the two nonequivalent water molecules in
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20 the stretched equilibrium geometry, when each considered as an isolated system, have dipole
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22 moments approximately 5% lower with MP2 and CCSD(T) than with HF. Since HF
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24 overestimates the dipole moments, it will also overestimate the strength of the attraction between
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26 them. When post HF methods correct the dipoles downward, they will also calculate a
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28 correspondingly lower binding energy.
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34 To test this numerically, the difference between the dipole–dipole interactions of HF and MP2,
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36 given the dipole strengths in Table 1 and the orientation of the molecules, is equal to 38.035
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38 $(\text{kJ/mol}) \cdot \text{\AA}^3 / R^3$. The plot of this function is depicted in Figure 5 along with the CBE curve for
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40 the stretched equilibrium geometry in the long range. The two curves coincide almost perfectly
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42 beyond 10 Å of separation and diverge only in the short range, where other correlation effects
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44 such as dispersion and charge transfer become comparably important. Further support for this
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46 electrostatic explanation comes from the relative behaviors of the four geometries. The aligned
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48 geometry displays positive CBE to a greater extent than the stretched equilibrium geometry, as
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50 its greater dipole interaction would lead us to expect, while the perpendicular geometry does not
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display it at all, because of its lack of a dipole–dipole interaction. The anti-aligned geometry is discussed below.

Table 1. Dipole moments (in debye) for the two water molecules in the stretched equilibrium geometry with three different methods.

	Water molecule 1	Water molecule 2
HF	1.986	1.981
MP2	1.867	1.863
CCSD(T)	1.879	1.875

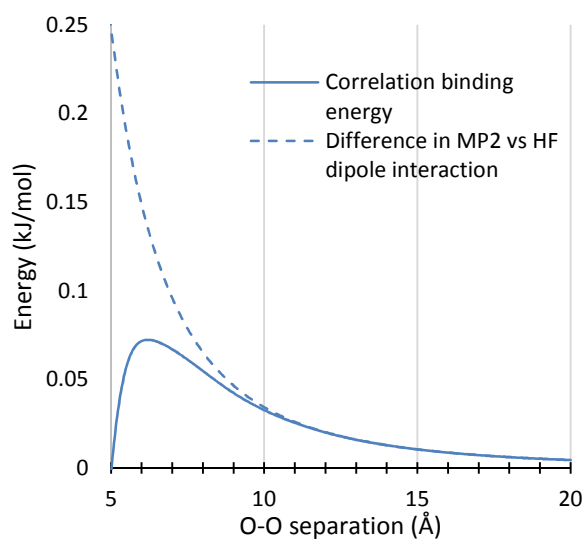


Figure 5. Correlation binding energy of the water dimer in the stretched equilibrium geometry vs. difference in dipole interaction from HF to MP2. As the center of the charge distribution does not affect the dipole moment, the centers of the charge distributions are chosen to be 0.35 \AA farther apart than the O-O separation.

Further confirmation can be obtained from the anti-aligned geometry. The situation for this geometry is the opposite of the aligned one: a large negative CBE instead of a large positive one, though the decay should still be as the inverse cube of intermolecular separation in the long range. To confirm this, the CBE was plotted against separation on a log-log plot, as seen in figure 6. As expected, the plot tends to a line with slope -3 , indicating inverse cubic decay. The aligned geometry converges to a line parallel to that of the anti-aligned geometry. The fact that their signs are opposite is not visible on the log-log plot. That the two very different curves converge to something so similar indicates the same effect is behind the long range behavior for both geometries, and the slope being -3 confirms that this effect is electrostatic.

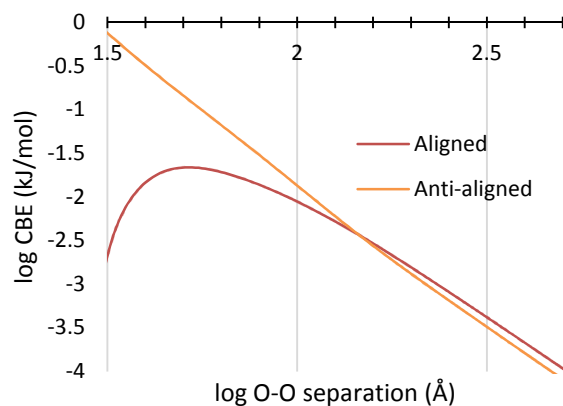


Figure 6. Log-log plot (natural logarithm) of absolute value of CBE for water in the aligned and anti-aligned geometries.

It seems safe to conclude that the positive correlation binding energy in the stretched equilibrium and aligned geometries of the water dimer is because of a post HF correction to the electrostatic interactions in the system. The electrostatic correction can be more important than dispersion in the long range, and causes the CBE to have two properties very different from

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3 dispersion: being anti-binding in nature and having a long-range decay as the inverse cube of
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5 separation, rather than the inverse sixth power.
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8 While we have illustrated the effect for the water dimer, it will be widespread because the
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10 tendency for the HF method to overestimate dipole moments is fairly general. For example,
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12 taking the dipole–dipole bound small intermolecular complexes from the A24 data set, as
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14 summarized in Table 2 below, we see that the CBE is uniformly negative at the equilibrium
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16 geometry and uniformly positive at a sufficiently stretched geometry. For four of the systems,
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18 this occurs by 3 Å, though for the ammonia dimer, it happens only at a larger separation. In
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20 contrast, for the methane dimer, an example nonpolar system, the CBE is -4.231 kJ/mol at
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22 equilibrium and remains negative at all separations, being -0.09984 kJ/mol at 3 Å beyond
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24 equilibrium and -0.00512 kJ/mol at 7 Å. Thus, binding correlation effects which become
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26 dispersive at large separations are dominant at the equilibrium separation, while anti-binding
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28 correlation corrections to HF-level electrostatic interactions can become dominant in the longer
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30 range.
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39 **Table 2.** Correlation contributions to the intermolecular interaction
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41 energies of small complexes from the A24 database, evaluated at
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43 the equilibrium geometry and at a geometry where the monomers
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45 are translated apart by $3/7$ Å. RIMP2 is used with the aug-cc-
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47 pVQZ basis set and the corresponding auxiliary basis, without
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49 counterpoise correction and with the frozen core approximation.
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51 Values in parentheses are evaluated via attenuated RIMP2 with the
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aug-cc-pVTZ basis set: RIMP2(terfc, aTZ), also with the frozen core approximation.

	ΔE_{corr} (R_e) (kJ/mol)	ΔE_{corr} ($R_e+3\text{\AA}$) (kJ/mol)	ΔE_{corr} ($R_e+7\text{\AA}$) (kJ/mol)
water–ammonia	−9.041 (−9.119)	0.01982 (0.08533)	0.02448 (0.02679)
HF dimer	−3.212 (−3.656)	0.1153 (0.1377)	0.02821 (0.03046)
HCN dimer	−4.106 (−4.136)	0.3424 (0.3614)	0.1275 (0.1241)
ammonia dimer	−7.240 (−6.827)	−0.06488 (0.00855)	0.00541 (0.00774)
formaldehyde dimer	−9.054 (−7.909)	0.4988 (0.6469)	0.1260 (0.1296)

The general result of this work is that intermolecular interactions at long range are often reduced, rather than increased, by the inclusion of electron correlation as a consequence of correcting the overly large permanent dipole moments of the Hartree–Fock model. As a result, the long-range distance dependence of the correlation contribution to the binding energy is often much stronger than the R^{-6} of true dispersion interactions: it may go instead as the leading contribution of electrostatic moments that are not correctly described by the HF reference. Hence the long-range contribution of correlation to intermolecular interactions has a leading distance dependence of R^{-3} in the water dimer, and it can go as slowly as R^{-2} for the case of an ion–dipole complex such as $\text{Na}^+ \dots \text{H}_2\text{O}$.

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3 Attenuated MP2 methods^{16,17,40,41} have recently attracted attention because smooth removal of
4 long-range correlation can cancel basis set superposition errors and erroneous C_6 values in
5 stacking complexes, and yield much more accurate intermolecular interaction energies than
6 conventional MP2 in the same basis set. Since the correlation potential is damped to zero at long
7 range, it may be reasonable to assume that the leading correlation contribution to intermolecular
8 interactions is lost upon attenuation. We demonstrate, perhaps surprisingly, that this is often not
9 true. As shown in Table 2, the MP2(terfc, aTZ) results do correctly recover the long-range
10 interaction energy in many intermolecular complexes, because that interaction is not dispersive.
11 The correlation correction to an A–B intermolecular electrostatic interactions is retained in
12 attenuated MP2 because it *implicitly* enters the short-range correlation energy expression through
13 changes in the orbital eigenvalues of molecule A (and B) due to the long-range electrostatic
14 perturbation of molecule B (and A). In turn this changes the monomer correlation energies, even
15 if the *explicit* intermolecular correlation terms (dispersive in nature) are damped to zero.
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34 A different approach is used in Hartree–Fock plus dispersion (HFD) methods⁴², which have
35 lately been the subject of renewed interest.^{43,44} These methods add an R^{-6} dispersion term to the
36 HF intermolecular interaction and stand in contrast to attenuated MP2. Whereas attenuated MP2
37 includes only short range correlation, HFD attempts to account for only long range correlation.
38 However, most HFD methods only modify HF by the addition of dispersion and HF
39 electrostatics unmodified. Therefore, unlike attenuated MP2, they cannot correctly describe the
40 long range behavior of dipole-bound systems. An exception is the HFDC method^{43,44} of Szalewicz
41 *et. al.*, which also computes on-molecule correlation, allowing it to describe the electrostatics
42 correctly. A more typical recent HFD approach is described by Iwata, which accounts for
43 dispersion by including only intermolecular correlation^{44,45}. He observed that polar systems were
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3 over-bound; the results presented here show that the explanation is the overestimation of HF
4 dipole moments, with the error growing more pronounced in the long range. His HFD method
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6 does not include the post-HF electrostatic corrections discussed here.
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10 The same considerations also have implications for energy decomposition analysis (EDA)
11 methods that partition an intermolecular interaction into physically motivated components. For
12 any post-HF EDA that includes correlation to be fully satisfactory, it should include terms
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14 correcting the permanent — as well as induced — electrostatics of the mean field HF reference.
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16 Failure to do so^{18,21,29} means ignoring an effect that can be more important than dispersion in the
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18 long range, and that becomes increasingly significant (though no longer dominant) in the short
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20 range. We are currently working on an EDA for MP2 that partitions the correlation energy into
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22 terms including corrections to the HF electrostatics and polarization and hope to present results
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Notes

The authors declare no competing financial interests.

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