Characterizing the Potential Energy Surface of the Water Dimer with DFT: Failures of Some Popular Functionals for Hydrogen Bonding

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Ten stationary points on the water dimer potential energy surface have been examined with ten density functional methods (X3LYP, B3LYP, B971, B98, MPWLYP, PBE1PBE, PBE, MPW1K, B3P86, and BHandHLYP). Geometry optimizations and vibrational frequency calculations were carried out with the TZ2P-(f,d)+dif basis set. All ten of the density functionals correctly describe the relative energies of the ten stationary points. However, correctly describing the curvature of the potential energy surface is far more difficult. Only one functional (BHandHLYP) reproduces the number of imaginary frequencies from CCSD(T) calculations. The other nine density functionals fail to correctly characterize the nature of at least one of the ten $(H_2O)_2$ stationary points studied here.

1. Introduction

While density functional theory (DFT) is arguably the most popular electronic structure technique for large molecules or molecular clusters, the development of functionals that can reliably describe weak interactions (e.g., hydrogen bonding and van der Waals forces) continues to be a very active area of research.[1−8] Several groups have identified a few DFT approaches that can accurately describe the energetics of small water clusters that range in size from $(H_2O)_2$ to $(H_2O)_{19}$.[9−12] However, if DFT methods are to be trusted to explore the topologically diverse potential energy hypersurfaces (PESs) of water clusters and solvated systems, the functionals must not only identify key stationary points but also correctly characterize the curvature of the PES at those points.

Several recent papers have identified density functional methods that are able to accurately describe the energetics of hydrogen bonding in a variety of systems including water clusters and even water/amino acid complexes.[13−15] Based on recommendations from these systematic studies, ten functionals (PBE, PBE1PBE, B3P86, MPW1K, B971, BHandHLYP, X3LYP, B3LYP, B98, and MPWLYP) have been applied to examine the PES of the simplest water cluster, $(H_2O)_2$. Notably, most of these functionals are hybrid GGAs. The DFT structures, relative energies, and vibrational frequencies of ten stationary points on the $(H_2O)_2$ PES are compared to existing CCSD(T) results.[16]

2. Theoretical Methods

The ten stationary points on the water dimer PES (shown in Figure 1) were optimized with ten different density functionals (B3LYP,[17,18] X3LYP,[19] B971,[20] B98,[21] MPWLYP,[18,22] PBE1PBE,[23,24] PBE,[23] MPW1K,[25] B3P86,[17,26] and BHandHLYP[18,27,28]). All calculations employed a triple-ζ basis set augmented with two sets of polarization functions on each H and O atom, a set of 5d-like higher angular momentum functions on each H atom and a set of 7f-like higher angular momentum functions on each O atom, a set of s-like and p-like diffuse functions for each O atom, and an s-like diffuse function for each H atom (denoted TZ2P(f,d)+dif, described in detail elsewhere[16] and in the Supporting Information).

Each structure was optimized in the point group listed in Figure 1. Optimized Cartesian coordinates obtained with all ten functionals are available in the Supporting Information. Unscaled harmonic vibrational frequencies, also available in the Supporting Information, were computed via analytic second derivatives to confirm the nature of each stationary point and compared to the Hessian index (number of imaginary frequencies) from published CCSD(T) calculations.[16]

Relative electronic energies of the stationary points (ΔE_e) are defined with respect to the global minimum structure 1 (nonplanar open C_s). No counterpoise corrections[29,30] were performed because energies are compared to the global minimum rather than two infinitely separated water monomers, and by definition, there is no intermolecular basis set superposition error.[31] All computations performed in the present study were carried out with the *Gaussian 03*[32] quantum chemistry software package, except calculations involving the MPW1K, X3LYP, and B3LYP functionals, which were performed with the NWChem4.6[33,34] quantum chemistry software package. The default numerical integration grid was employed when using *Gaussian 03*, which consists of a pruned grid with 75 radial shells and 302 angular points. To compute energies to a target accuracy of 1×10^{-8} E_h, the xfine grid was used in NWChem4.6 (100 radial shells and 1202 angular points per shell for H and 100 radial shells and 1454 angular points per shell for O).

Finally, we note that, although the CCSD(T) vibrational frequencies reported in ref 16 were obtained via finite differences of gradients, we have confirmed the results with the analytic second derivatives available in ACES2.[35] The number of imaginary frequencies is the same for both procedures, and the magnitudes of the vibrational frequencies change by no more than 2 cm^{-1} in the worst case (for structure **10**) and by no more than 0.6 cm^{-1} in all other cases. In addition, these CCSD(T) Hessian indices agree with an earlier study that reported MP2 analytic frequencies with the 6-31+G(d,p) basis set.[36]

3. Results and Discussion

The structures of ten stationary points on the water dimer potential energy surface are displayed in Figure 1. Qualitatively,

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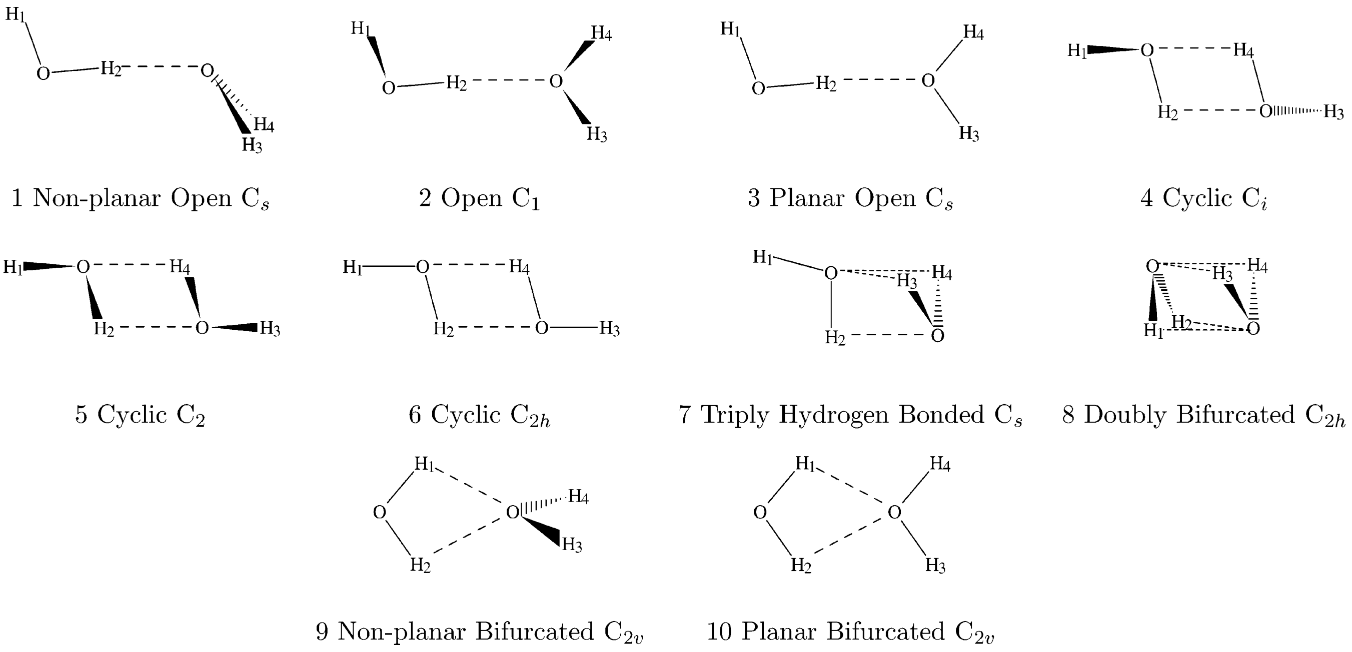
1 Non-planar Open C_s

2 Open C_1

3 Planar Open C_s

4 Cyclic C_i

5 Cyclic C_2

6 Cyclic C_{2h}

7 Triply Hydrogen Bonded C_s

8 Doubly Bifurcated C_{2h}

9 Non-planar Bifurcated C_{2v}

10 Planar Bifurcated C_{2v}

Figure 1. The structures of all ten stationary points studied on the $(H_2O)_2$ intermolecular potential energy surface. O_1 is implicitly associated with the monomer containing H_1 and H_2, while O_2 is similarly associated with H_3 and H_4.

TABLE 1: Oxygen−Oxygen Bond Lengths (in Å) of the Ten Water Dimer Stationary Points Studied[a]

method	1	2	3	4	5	6	7	8	9	10	AAE
CCSD(T)[b]	2.91	2.92	2.93	2.82	2.79	2.79	2.94	3.29	3.01	3.18	0.00
B3LYP	2.92	2.94	2.94	2.85	2.80	2.80	3.00	3.39	3.06	3.25	0.04
X3LYP	2.91	2.92	2.92	2.83	2.82	2.78	2.97	3.33	3.03	3.20	0.02
B971	2.92	2.94	2.94	2.86	2.84	2.80	2.99	3.03	3.06	3.20	0.05
B98	2.92	2.94	2.95	2.87	2.85	2.82	3.00	3.39	3.06	3.24	0.05
MPWLYP	2.93	2.93	2.94	2.85	2.85	2.81	3.00	3.35	3.06	3.25	0.04
PBE1PBE	2.89	2.91	2.92	2.83	2.83	2.80	2.97	3.30	3.03	3.20	0.02
PBE	2.90	2.92	2.92	2.85	2.85	2.80	3.00	3.33	3.04	3.25	0.03
MPW1K	2.89	2.91	2.91	2.83	2.84	2.79	3.01	3.39	3.05	3.25	0.04
B3P86	2.87	2.89	2.89	2.82	2.81	2.76	2.94	3.39	3.02	3.22	0.03
BHandHLYP	2.90	2.91	2.91	2.82	2.79	2.76	2.94	3.30	3.01	3.17	0.01

[a] Average absolute errors (AAE) of the DFT O−O bond lengths with respect to the CCSD(T) values are reported in the last column. All data obtained with the TZ2P(f,d)+dif basis set. [b] CCSD(T) values from ref 16.

TABLE 2: Relative Electronic Energies (ΔE_e, kcal mol^{-1}) of the Ten Water Dimer Stationary Points Studied[a]

method	1	2	3	4	5	6	7	8	9	10	AAE
best est.[b]	0.00	0.52	0.57	0.70	0.95	0.99	1.81	3.57	1.79	2.71	0.00
CCSD(T)[c]	0.00	0.57	0.65	0.85	1.13	1.20	1.91	3.62	1.83	2.83	0.10
B3LYP	0.00	0.58	0.64	1.05	1.35	1.49	2.14	3.67	1.98	2.87	0.24
X3LYP	0.00	0.58	0.65	1.01	1.31	1.44	2.17	3.81	2.02	2.98	0.26
B971	0.00	0.58	0.67	0.95	0.67	1.41	1.98	3.53	1.85	2.77	0.16
B98	0.00	0.58	0.65	1.00	1.30	1.44	2.00	3.49	1.85	2.73	0.18
MPWLYP	0.00	0.60	0.73	1.03	1.35	1.58	2.20	3.77	2.07	3.02	0.31
PBE1PBE	0.00	0.61	0.71	1.04	1.36	1.54	2.15	3.73	2.01	2.94	0.28
PBE	0.00	0.66	0.84	1.06	1.41	1.75	2.26	3.75	2.12	3.08	0.37
MPW1K	0.00	0.59	0.63	1.07	1.38	1.50	2.04	3.63	1.95	2.81	0.22
B3P86	0.00	0.65	0.77	1.17	1.50	1.77	2.37	3.88	2.20	3.13	0.42
BHandHLYP	0.00	0.52	0.54	0.94	1.19	1.24	2.06	3.81	1.93	2.88	0.17

[a] Average absolute errors (AAE) of the CCSD(T) and DFT energies with respect to the literature best estimate values are reported in the last column. All data obtained with the TZ2P(f,d)+dif basis set. [b] Best estimate literature values from ref 16. [c] CCSD(T) values from ref 16.

very little difference exists between the structures optimized with these ten DFT methods and the CCSD(T) structures obtained with the same basis set in ref 16. On average, the O−O bond lengths are within 0.05 Å of the CCSD(T) values for all ten functionals, as reported in Table 1. Optimized Cartesian coordinates are available in the Supporting Information to facilitate comparison of other geometrical parameters.

The energies of the water dimer structures relative to the energy of the global minimum (as seen in Table 2) show that all of the density functionals reproduce the energetic ordering at the best estimate literature and CCSD(T) levels.[16] Quantitatively, three functionals have an AAE between 0.15 and 0.20 kcal mol^{-1}, four functionals have an AAE ranging from 0.21 to 0.30 kcal mol^{-1}, two have an AAE between 0.31 and 0.40 kcal/mol, and the remaining functional has an AAE of 0.42 kcal mol^{-1}. These results are consistent with recent systematic studies of density functionals for hydrogen bonding.[13,14]

Despite providing fairly reliable structures and relative energies, most of the density functional methods examined do not correctly characterize the curvature of the PES. Only one

TABLE 3: Number of Imaginary Vibrational Frequencies (n_i) Associated with the Ten Water Dimer Stationary Points[a]

method	1	2	3	4	5	6	7	8	9	10
CCSD(T)[b]	0	1	2	1	2	3	2	3	1	2
B3LYP	0	1	2	1	**1**	3	2	3	1	2
X3LYP	0	1	2	1	**1**	3	**1**	3	1	2
B971	0	1	2	1	**1**	3	2	3	1	**3**
B98	0	1	2	1	**1**	**2**	2	3	1	2
MPWLYP	0	1	2	1	**1**	3	2	3	1	**3**
PBE1PBE	0	1	2	1	**1**	3	2	3	1	2
PBE	0	1	2	1	**1**	3	2	3	1	2
MPW1K	0	1	2	1	**1**	3	**1**	3	1	2
B3P86	0	1	2	1	**1**	3	2	3	1	**3**
BHandHLYP	0	1	2	1	2	3	2	3	1	2

[a] Bold indicates a frequency which does not agree with the literature values in row one. All data obtained with the TZ2P(f,d)+dif basis set unless otherwise noted. [b] CCSD(T) values from ref 16.

density functional method was able to correctly reproduce the CCSD(T)[16] Hessian indices of all ten stationary points studied, as reported in Table 3. The functional BHandHLYP correctly characterized all ten stationary points. B3LYP, PBE, and PBE1PBE each incorrectly identified the number of imaginary vibrational frequencies associated with structure **5**, while each of the six remaining functionals incorrectly characterized structure **5** along with either structure **6**, **7**, or **10**. Although one should not draw broad conclusions from such a small test set, it can be noted that the hybrid functionals tend to perform quite well and generally only fail for structure **5**.

Of the 15 discrepancies, 9 were associated with structure **5**, which has imaginary frequencies of 119.3i cm^{-1} and 33.5i cm^{-1} at the CCSD(T) level. Since the magnitude of the latter value is quite small, the unscaled harmonic vibrational frequencies have been included in the Supporting Information to demonstrate that the incorrect values not only have the wrong sign but also are significantly different than zero. For example, calculations with all but one of the DFT methods indicate that structure **5** is a transition state. For the B3LYP functional, the imaginary mode has a magnitude of 159.6i cm^{-1}, while the smallest real frequency is 82.0 cm^{-1}. The corresponding values for the PBE1PBE functional are 162.1i cm^{-1} and 99.8 cm^{-1}. These values do not change substantially when more dense numerical integration grids are employed. When the *Gaussian 03* numerical integration grid was increased to 99 radial shells and 974 angular points per shell, the B3LYP values changed by no more than 2.7 cm^{-1} and the PBE1PBE values by no more than 3.1 cm^{-1}.

The magnitudes of the vibrational frequencies in hydrogen-bonded systems can also be rather sensitive to basis set.[37] To test this dependence, CCSD(T) frequencies have also been computed for structure **5** with a with triple-ζ correlation consistent basis set augmented with diffuse functions on the O atoms (cc-pVTZ for H and aug-cc-pVTZ for O).[38,39] The CCSD(T) imaginary frequency of 33.5i cm^{-1} associated with structure **5** changes to 58.5i cm^{-1} when the TZ2P(f,d)+dif basis is replaced with this much larger correlation consistent basis set. Although this is a large relative change, it does not affect the nature of the stationary point.

4. Conclusions

Ten density functionals (X3LYP, B3LYP, B971, B98, MPWLYP, PBE1PBE, PBE, MPW1K, B3P86, and BHandHLYP) were used to examine ten stationary points on the PES of the water dimer. Full geometry optimizations of the ten water dimer structures were performed with each of the ten DFT methods. These density functionals were also used to compute relative electronic energies and harmonic vibrational frequencies for each of the stationary points.

The density functionals provide reliable structures; geometrical parameters from the DFT optimized structures are very similar to those from CCSD(T) computations. The density functionals also provide reliable relative energies. All ten functionals correctly describe the relative energies of the ten stationary points and are within a few tenths of a kilocalorie per mole of the CCSD(T) data on average. However, most functionals do not correctly characterize the nature of stationary points. The hybrid functionals tend to fail only for structure **5**, and the BHandHLYP hybrid functional is the only one that correctly reproduces the number of imaginary frequencies for all ten water dimer stationary points. However, with such a small test set, it is not possible to draw conclusions about the general performance of these functions for hydrogen-bonded systems. We are in the process of extending this study to larger water clusters. However, this arduous task will take some time to complete, since few, if any, benchmark frequencies exist for stationary points on the potential energy surfaces of $(H_2O)_3$, $(H_2O)_4$, and $(H_2O)_5$.

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Supporting Information Available: Unscaled harmonic vibrational frequencies, Cartesian coordinates, and details of the TZ2P(f,d)+dif basis set. This material is available free of charge via the Internet at http://pubs.acs.org.

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