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AM05 Density Functional Applied to the Water Molecule, Dimer, and Bulk Liquid[†]

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Abstract: We compare results for water obtained with the AM05 exchange-correlation density functional (Armiento, R.; Mattsson, A. E. *Phys. Rev. B* **2005**, *72*, 085108) with those obtained with five other pure functionals: LDA, PBE, PBEsol, RPBE, and BLYP. For liquid water, AM05 yields an O–O pair correlation function that is more structured than the ones of PBE and BLYP, which, in turn, are more structured than the one of RPBE. However, LDA and PBEsol yields more structured water than AM05. We show that AM05 yields a H_2O dimer binding energy of 4.9 kcal/mol. The result is thus within 0.15 kcal/mol of CCSD(T) level theory (5.02 ± 0.05 kcal/mol). We confirm that accuracy in the water dimer binding energy is not a strong indicator for the fidelity of the resulting structure of liquid water.

1. Introduction

Quantitative results for a broad range of systems in combination with a relatively low computational cost has made density functional theory (DFT)[1,2] the foundation of most large-scale quantum mechanical simulations. The limiting factor for the accuracy of the calculations is the approximation for the exchange-correlation (XC) functional. While the local density approximation (LDA) functional, proposed in early DFT works, gives resonably accurate properties for solid-state systems, the application of DFT to systems of interest in chemistry did not emerge until more advanced functionals were constructed, work where John Perdew and co-workers have been instrumental. Today, for single character systems, like bulk solids or strictly molecular systems, the wide use of DFT is a testament to the theory's advantages. The use of XC functionals is, however, largely divided depending on the application. In fact, only a few functionals, among them the Perdew–Burke–Ernzerhof (PBE) functional,[3] are extensively used for both solid and molecular systems. The quest for even more accurate

functionals has been most vigorously pursued for chemistry applications, and for high accuracy in molecular systems the use of hybrid functionals is now considered vital. For solids, local and semilocal functionals, such as LDA and different general gradient approximations (GGAs), such as PBE, are mostly employed even though, also here, more accurate functionals have been developed lately.

For some time,[4] it has been evident that one of the largest challenges in the field resides in developing a functional that can bridge the gap between molecular and solid systems. Thus, the performance of several hybrid functionals have recently been investigated for solid-state systems (see for example refs 5 and 6), sometimes with very good results. However, in addition to accuracy, the speed of the calculation has emerged as an additional major consideration: DFT is increasingly being employed for larger systems and for longer molecular dynamics (MD) simulations, both applications requiring as fast functional evaluations as possible. While some hybrids are accurate for solid-state systems, the computational overhead compared to a GGA type functional is prohibiting for these applications. In a recent study,[7] we showed that the Armiento and Mattsson functional of 2005 (AM05),[8] while being of the fast GGA type preferred in large calculations, is as accurate as the best hybrids for solid-state systems.

There is thus ample motivation to investigate the performance of the AM05 functional[8] for molecules and liquids. Our focus here is on the structure of liquid water. We also calculate the structure and binding energy of the water dimer because it explores the hydrogen bonding pertinent to the liquid water structure. The chemical bonding in the water molecule is only explored via the structure; a more extensive study of molecules using AM05 will be published elsewhere.[9]

We, in addition to AM05, for benchmarking purposes include three GGA type functionals commonly used in studies of molecular systems in general and water in particular: BLYP,[10,11] RPBE,[12] and PBE.[3] These functionals are shown to not perform as well as AM05 for solids,[7] but they have reasonable performace for molecular systems and are thus the preferred functionals for applications, such as liquid water, requiring a fast functional.

Although not normally used for water, we also include LDA in the comparisons. First, LDA plays an important role in elucidating the differences between functionals. For example, AM05 is a subsystem functional; it is made to reproduce the exact combined XC energy for two reference systems, the uniform electron gas and the jellium surface. AM05 thus shares one of its reference systems, the uniform electron gas, with LDA. A main conclusion of this work is that AM05 does not share the deficiencies of LDA for molecular systems. Second, LDA performs very well for a number of heavy transition metals; see for example ref 7. When studying the interface between molecules and solids, it is important that the properties of *both* the solid and the molecular components are taken into account accurately. When deciding on which functional to use for heterogeneous systems, it is important to know not only how well a functional performs for one component (LDA describes Pt well) but also how poorly it performs for the other (LDA overbinds molecules significantly).

The recently constructed PBEsol[13] functional yields almost exactly the same lattice constants and bulk moduli as AM05, for important and large classes of solids.[14−16] Results also agree for other properties,[17] but sometimes differences have been shown.[18] Despite mostly giving the same results as AM05, PBEsol is constructed according to very different principles than AM05. In particular, PBEsol is not expected to give good molecular properties.[13] In contrast, nothing in the construction of AM05 would prevent it from performing well also for molecules. It is thus interesting to compare the performance of PBEsol to that of AM05 also for systems of less solid-state character, and we therefore include PBEsol in this comparison.

Another functional that we would have liked to compare results with for the studied systems is the meta-GGA functional of Tao, Perdew, Staroverov, and Scuseria[19] (TPSS). However, TPSS is not available in the code we use and is not readily implemented in it. But others have used TPSS in studies[20,21] comparable to ours. Even though it is not advisable to compare too closely results obtained by very different codes, some information can be extracted by relating results for the common functionals (in this case PBE and BLYP) in two studies to the functional of interest (here

TPSS). We are thus able to, to some extent, relate results otained by others with TPSS to those obtained here using AM05.

In this study we focus on pure functionals. However, in the chemistry community there is a considerable interest in hybrid functionals in general and the B3LYP functional in particular. In the same way as we are able to compare TPSS results by others to our results for pure functionals, as described above, we are also able to compare B3LYP results obtained by others for the water dimer. Liquid water radial distrubution functions have been calculated using hybrid functionals (see for example ref 27), but we have not found a B3LYP study that can be compared to ours. We also note that B3LYP performs slightly worse than PBE for solids.[6]

2. Method

First-principles simulations involve a number of approximations, fundamental as well as technical. Because the purpose of functional development is to improve the fundamental accuracy of the theory, it is particularly important to maintain the best possible technical precision in calculations for the purpose of functional development. The accuracy of contemporary exchange-correlation functionals has raised the requirements for overall precision.

2.1. XC Functionals. In the Kohn−Sham DFT computational scheme[2] the ground-state electron energy is obtained via the solution of the Kohn−Sham (KS) equations. Although all many-body effects can *formally* be accounted for within the XC functional, the crucial question is how good the approximation of this quantity is.

As discussed above, PBE[3] gives reasonable accuracy for both molecular and solid-state systems, and it has been tested and used extensively in calculations for large classes of different materials and properties. Even though there are more accurate functionals for specific materials, it appears to be the functional with most broad range performance. In contrast, the BLYP and RPBE functionals show unsatisfactory performance for solid-state systems[7] while they perform well for molecular systems. PBE and BLYP are both used extensively for water,[20,22−30] and RPBE has been suggested to give a water structure in good agreement with experimental results.[23] While the performance of LDA lies between that of the PBE and the BLYP/RPBE functionals for solid-state systems,[7] LDA is well-known to give too structured water. AM05 and PBEsol perform very well for solid-state systems, but they have not previously been tested for water. A brief review of the functionals used in this study was presented in ref 7. Here we only discuss AM05 because it is the main topic of this paper.

Kohn and Mattsson discussed the creation of an XC functional from a surface-oriented model system and its possible combination with another treatment where this model was unsuitable.[31,32] The approach was formalized and generalized in the subsystem functional scheme by Armiento and Mattsson.[33] The fundamental idea is to create several separate subsystem functionals, each accurately describing a specific model system, and then use an interpolation function[34] that based on the nature of the real system in each point determines how much of each subsystem functional

to use in this point. Because LDA is based on the uniform electron gas model system, it is a subsystem functional and can be easily incorporated in the subsystem functional scheme. The ideas of the subsystem functional scheme were made concrete in the AM05 functional.[8] Subsystem functionals based on two model systems are used: the LDA functional based on the uniform electron gas and a surface functional derived from the Airy gas[31] in combination with the jellium surfaces.[35] The interpolation function is based on the magnitude of the dimensionless gradient:[8] If the dimensionless gradient of the real system is large, the system in this point is surface-like, while if it is small, the system is more uniform electron gas like.

The AM05 surface exchange functional is a parametrization of the Airy electron gas data.[31] For correlation, Armiento and Mattsson derived a semicompatible surface correlation from the XC data available for jellium surface models, based on the idea that both the Airy gas and jellium surface models are related to similar surface physics.

Note that AM05 stems from a completely different theoretical framework than functionals originally referred to as GGAs. The subsystem functional scheme is not based on gradient expansions, and thus AM05 is "not a GGA" in the theoretical sense. However, it is of the same form as a GGA and can be easily implemented in a code using the same input quantities as, e.g., PBE does.[16]

The AM05 functional is the first functional constructed according to the subsystem functional scheme. It can be seen as a consistent theoretical improvement over LDA because it reproduces the exact XC energy for *two* types of model systems, the uniform electron gas *and* the jellium surfaces, describing two situations with fundamentally different physics. The subsystem functional scheme offers a promising alternative approach to further improved functionals, by exploiting exact XC model systems and adding them to the ones already reproduced.

Applying AM05 to water in the current work (see Table 2), we see how this formal theoretical improvement over LDA translates into significantly improved numerical results for molecular systems. Because AM05 and traditional GGA functionals are constructed according to such different philosophies, traditional theoretical comparisons are hard to make.[13,14] Performanace assessments of AM05 compared to other GGA functionals have to be based on results from high-precision calculations.

2.2. Numerical Precision. While the XC functional determines the fundamental *accuracy* of the calculation, there is a second source of errors, the numerical *precision* in solving the Kohn−Sham equations. The numerical precision is determined by implementation-related approximations, such as choice of basis sets, pseudopotential quality, approximate matrix diagonalization methods, plane-wave cutoff energies, etc. (see ref 36). In general, the precision can be successively improved by increasing the computational expense (i.e., by converging the calculations).

The concept of precision is particularly important in the area of functional development. When the differences between functionals are small,[37] the precision of the calculations has to be high enough to resolve them.

In this study we use the pseudopotential, plane-wave VASP 5.1 code,[5,38−40] with projected augmented wave (PAW) core potentials,[41,40] ported to the Cray platform.[42] In a recent publication,[28] it was shown that with appropriate settings, VASP yields high precision MD results for water.

The PAW implementation in VASP 5.1 allows use of multiple XC functionals on the same set of core potentials[40] while retaining high precision. The difference in AM05 results using existing LDA or PBE core potentials in VASP 5.1 has been carefully studied[7] and shown to be minimal. In this study we use PBE core potentials for all functionals except LDA, where the LDA core potentials are used instead.

Pseudopotentials should reproduce the results of all-electron calculations. The VASP PAW core potentials have been extensively evaluated (see for example refs 5 and 7) and are of high quality. However, because we want to have good control over numerical errors in this study, we nevertheless consider transferability errors. Transferability can be improved by using a harder core potential, requiring a larger plane wave basis (cutoff). To investigate the effect of potential hardness, we used two types of PAW core potentials, one softer (nominally needing a 400 eV cutoff) and one harder (nominally needing a 700 eV cutoff), for a subset of the functionals tested, in the molecule and dimer calculations. For the more demanding MD calculations, we used the 400 eV potentials. Because the dimer binding energies differ a mere 0.2 kcal/mol between the 400 and 700 potentials, as seen in Table 2, they are unlikely to yield different results for the liquid structure. The water structures resulting from the two different core potentials are indeed very similar, as shown in ref 28.

In order to minimize the possibility that numerical errors obscure the differences between functionals, we use more stringent than normal settings in all our calculations. To minimize interactions with periodic copies, a cubic cell with 12 Å sides is used for the molecule and the dimer calculations. In the self-consistent loop, the convergence criterium is set to at least 1.0×10^{-5} eV. All calculations are gamma point only, and a 500 eV cutoff is used for the 400 eV potentials while the harder 700 eV potential calculations are done with a 1000 eV cutoff.

In order to minimize effects of system size, we study a cell of 64 water molecules. The simulations are performed in the NVT ensemble using a Nose thermostat,[44] deuterium mass, and the velocity verlet algorithm with a 0.5 fs time step. Because the average temperature is fixed, the energy shift due to time integration errors is absorbed in the thermostat degreee of freedom. The energy absorbed by the thermostat is of the order 1K/ps, see ref 28 for a more extensive discussion on basis set convergence, energy drift, and thermalization between hydrogen and oxygen degrees of freedom. The MD simulations are between 15 and 50 ps long, depending on temperature/rate of thermalization for the different functionals. As shown in Figure 4, the different functionals yield highly different structures for liquid water at 300 K. For example, while RPBE-water is liquid with rather rapid thermalization behavior already at 300 K, PBE and AM05-water are glassy with significant structure and long thermalization time. RPBE gives a pair correlation

Table 1. Properties of the Water Molecule, the OH Distance (R_{OH}), and the HOH Angle ($\angle$HOH), As Obtained with Six Functionals: AM05, PBE, LDA, PBEsol, BLYP, and RPBE, Compared to 'Best ab Initio'[49] (CCSD(T)), As Described in Ref 43[a]

| | R_{OH} (Å) | | $\angle$HOH (deg) | |
| | PAW | PAW | PAW | PAW |
functional	400 eV	700 eV	400 eV	700 eV
AM05	0.974	0.971	104.8	104.4
PBE	0.972	0.969	104.5	104.2
LDA	0.974	0.971	105.3	105.0
PBEsol	0.973		104.7	
BLYP	0.973		104.8	
RPBE	0.973		104.2	
best ab initio[49]	0.959		104.2	

^{a} For AM05, LDA, and PBE, results using two different sets of PAW core functions (labeled by their nominal energy cutoffs of 400 resp 700 eV, see text) are shown. The differences in results between the two sets is at the level of 0.3%, demonstrating that the softer potentials, employed in the MD simulations, also are of high fidelity.

function similar to ones extracted from experiments.[45−48] However, as will be discussed later, important effects not included in traditional DFT-MD simulations, like ours, call into question the relevance of direct comparisons to experimental findings.

We furthermore investigated the influence of initial state for AM05 and BLYP by annealing from structures equilibrated at higher temperature. The AM05-water was thermalized at 500 K and annealed to 300 K, followed by equilibration at 300 K. No significant difference in final structure was detected between this run and one continued from a PBE simulation. For BLYP, we went even further and investigated three different 400 K geometries followed by anneal to 300 K and 28, 22, and 24 ps simulations at 300 K. All three annealed runs eventually reached a structure similar to that of a BLYP run continued from a PBE final geometry as well as the PBE structure itself. Finally, the PBEsol simulations were continued from the corresponding final AM05 geometry. For all temperatures, the change to PBEsol resulted in a slightly more structured geometry.

3. Results

3.1. Water Monomer and Dimer. The results for molecular properties of water and the water dimer are presented in Table 1 and Table 2.

For the water monomer, the differences in results obtained with different functionals are small. AM05 lies between LDA and PBE, as is mostly the case for geometric properties like lattice constants.[7] The only significant difference is that LDA yields a slightly larger bond angle than the semilocal functionals. Overall, LDA performs as well for the water monomer as any of the semilocal functionals. However, none of the functionals tested here acheive the accuracy of hybrid functionals, that generally display a shorter OH distance, closer to the 'best ab initio' value.

Our results for the water dimer (see Figure 1) binding energies for PBE, BLYP, and LDA agree to within 0.1 kcal/mol to the energies reported by Xu and Goddard.[43] For the water dimer, LDA and PBEsol give a dimer binding energy
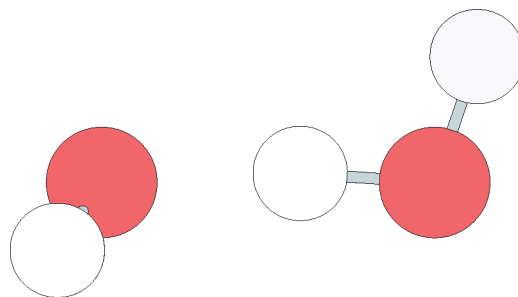

Figure 1. The water dimer. The R_{OO} value in Table 2 is the distance between the two oxygen atoms. ΔR_{OH} is the elongation of the O−H bond of the hydrogen binding hydrogen (the hydrogen atom between the two oxygens) compared to the O−H bond length in the monomer.

that is significantly too large, while BLYP and RPBE give that which is too small. AM05 and PBE both give dimer binding energies close to that of the best ab initio. That AM05 yields results close to those of PBE for this molecular system is interesting. A common view is that a functional constructed to perform well for solids, such as AM05 and PBEsol, would work less well than PBE for molecular systems.[13] The results for the water dimer clearly show that while this might be the case for PBEsol, this reasoning applies less well to functionals such as AM05, constructed according to the subsystem functional approach. It is also interesting to note that while AM05 gives geometrical dimer properties in between LDA and PBE, this is not the case for the binding energy of the dimer, where AM05 binds even less hard than PBE.

Water dimer binding energies and distances between oxygen atoms are calculated with several functionals in ref 21 among them TPSS, BLYP, and PBE. Our results for the binding energies for PBE and BLYP agree well with those results and we can thus conclude that the TPSS binding energy of 4.53 kcal/mol can be directly compared to our results, placing it slightly below the AM05 and PBE results. The agreement between the O−O distances calculated by us and in ref 21 is also good, and we can thus place the TPSS value of approximately 2.900 Å very close to the PBE value. Similar considerations place B3LYP results presented in ref 43 at 4.57 kcal/mol and 2.926 Å.

Figure 2 shows a summary of Table 2 and the TPSS results from ref 21 and the B3LYP results of ref 43, and AM05 and TPSS falls outside of trends drawn from the other pure functionals. For TPSS this is not too surprising because it is a meta-GGA and thus already by construction different from GGAs. That AM05 also falls outside of trends might be more surprising but is probably reflecting its very different theoretical foundation in the subsystem functional scheme. Figure 2 also shows the dramatic improvement AM05 gives compared to LDA for molecular systems, which is encouraging for using the subsystem functionals scheme, that relates LDA and AM05, for developing an even more accurate and generally applicable functional in the future.

3.2. Structure of Water. The importance of water as ubiquitous actor in the chemistry and biology of life can hardly be overestimated. An improved understanding of the interaction between water and ions, proteins, and solid

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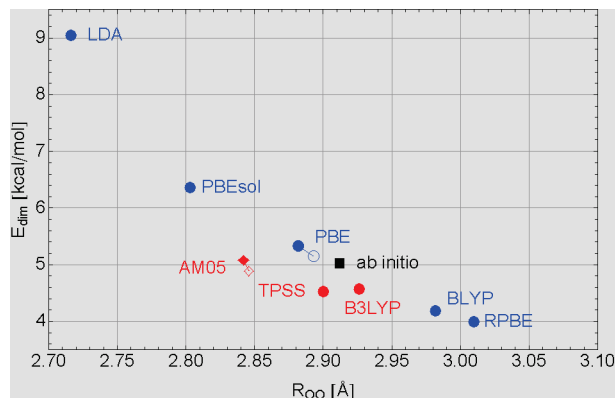
Figure 2. Dimer binding energy versus oxygen−oxygen distance, calculated with eight different functionals and compared to best ab initio (solid symbols). The TPSS results are taken from ref 21 and the B3LYP results from ref 43 For AM05 and PBE the calculations have also been performed with a harder PAW potential; those results are shown with open symbols. The numerical precision is significantly higher than the differences between functionals. Trends obtained by comparing LDA, PBEsol, PBE, BLYP, and RPBE cannot be applied to TPSS and AM05.

Table 2. Properties of the Water Dimer for Six Functionals: AM05, PBE, LDA, PBEsol, BLYP, and RPBE[a]

	E_{dim}, kcal/mol	R_{OO}, Å	ΔR_{OH}, Å
best ab initio[50]	5.02	2.912	0.006
AM05 (400)	5.08	2.842	0.013
AM05 (700)	4.89	2.846	0.013
PBE (400)	5.33	2.882	0.011
PBE (700)	5.15	2.893	0.011
LDA (400)	9.05	2.716	0.019
PBEsol (400)	6.36	2.803	0.015
BLYP (400)	4.19	2.982	0.008
RPBE (400)	3.99	3.010	0.007

[a] The properties are the dimer binding energy (E_{dim}), distance between the oxygen atoms (R_{OO}), and elongation of the hydrogen−oxygen bond compared to the water monomer (ΔR_{OH}), and they are compared to 'best ab initio'[50] (CCSD(T)), according to ref 43.

surfaces is hence highly sought. However, water is not only of importance in biochemistry, nanotechnology, and surface science/catalysis, but the structural and thermophysical properties of water under high energy-density conditions[51−54] largely determine the gravitational properties of water-rich giant planets like Neptune.[55] It is therefore not surprising that the structure of liquid water has been subject to intense theoretical efforts over the past few years.[20,23−30] The amount of recent work also suggests that the definitive consensus regarding first-principles simulation of water has not yet emerged.

For several reasons, liquid water is a particularly difficult system to study computationally. First, the low mass of the hydrogen (deuterium) atoms limits the molecular dynamics time step, making simulations over several tens of picoseconds computationally very demanding. Second, the mass ratio between oxygen and hydrogen atoms and the strong O−H bonds, in comparison to the weak hydrogen bonds, yields normal modes of very different frequencies, in turn, resulting in slow thermalization and sensitivity with respect to thermostats and equilibration times. Third, both hydrogen
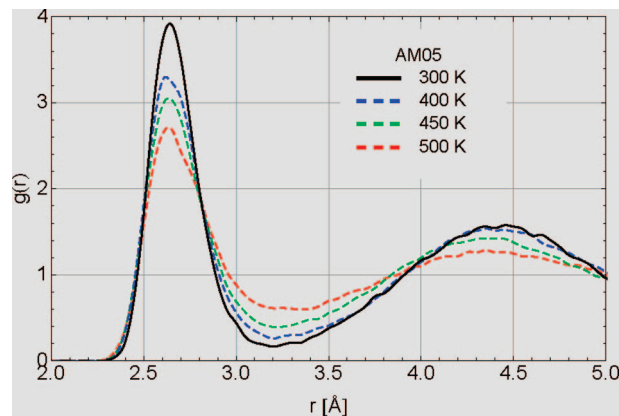
Figure 3. Oxygen−oxygen radial distribution function for AM05 as a function of temperature: 300 K (black), 400 K (blue dashed), 450 K (green dashed), and 500 K (red dashed).

and deuterium atoms are light enough to be influenced by quantum nuclei effects.[24,29] Fourth, long-range van der Waals/dispersion forces can be important in dense systems like liquid water.[30] None of the functionals included in this study is constructed with van der Waals/dispersion properties as a focus.

Taken together, there are thus good reasons to *avoid* liquid water as a system for benchmarking XC functionals. However, given the fundamental importance of liquid water, it is necessary to assess functional performance despite the technical challenges.

Our main result for AM05, the O−O pair correlation function, is presented in Figure 3. Just like PBE and LDA, AM05 yields overstructured liquid water at 300 K. As expected, the structure becomes less ordered with increased temperature. The overstructuring compared to experiment, however, remains also for higher temperatures.

Although the results for AM05 are the main focus of the paper, it is important to directly compare the functional's behavior to that of other functionals. The numerical challenges mentioned above limits the reliability of conclusions based only on comparisons with literature results. One example is the spread in average temperature resulting from NVE simulations; when changes in temperature of a few tens of Kelvin change the liquid structure, it is difficult to compare results with high confidence. In order to make as direct comparisons as possible, we therefore performed extensive additional simulations with other functionals using the same thermostats, timesteps, convergence criteria, etc.

In Figure 4, we compare the O−O pair-correlation function (radial distribution function) at 300 K for six different exchange-correlation functionals: AM05, PBE, LDA, PBE-sol, BLYP, and RPBE. The overall relative results for PBE, BLYP, and RPBE are in agreement with most previous simulations, for example those of refs 23, 24, and 20. In ref 20 O−O radial distribution function results are given for, among others, TPSS, BLYP, and PBE. While the differences between radial distribution functions obtained with the different functionals is suppressed by the different temperatures obtained in the NVE runs, it is clear that TPSS gives more structured water than PBE and BLYP. In the comparison in Figure 4, the O−O radial distribution function
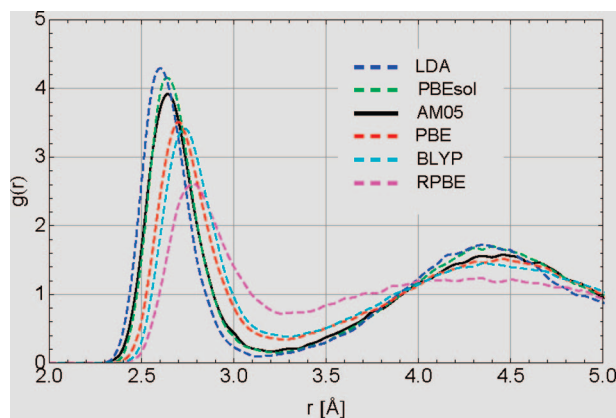
Figure 4. Oxygen−oxygen radial distribution function at 300 K for six functionals, in order of maximum peak height: LDA (blue dashed), PBEsol (green dashed), AM05 (black), PBE (red dashed), BLYP (turqoise dashed), and RPBE (purple dashed). The TPSS radial distribution function from Figure 8 of ref 20 would fall between AM05 and PBE. The structure of DFT water at 300 K thus ranges from very glassy (LDA) to liquid (RPBE) depending on the exchange-correlation functional used.

Figure 5. A measure related to the number of atoms in the first hydration shell versus the position of the maximum of the first peak (R_{max}, g_{max} is the maximum peak height). g_{max} and R_{max} for TPSS are estimated by comparing the TPSS, PBE, and BLYP radial distribution function from Figure 8 of ref 20 to the radial distribution functions for PBE and BLYP in Figure 4.

obtained with TPSS would end up between the PBE and the AM05 ones.

From the perspective of applying DFT as a first-principles theory, the results in Figure 4 can readily be interpreted as negative and even discouraging:[56] is there a reason to trust a theory where one can dial the answer for a property like the O−O pair correlation function simply by changing the XC functional? However, from a more fundamental point of view, the results are stimulating: which properties of the different functionals are responsible for their markedly different behavior, and how can one improve upon them?

It is clear from Figure 4 that the maximum peak heights are inversely proportional to the radial positions of the peaks. If the functionals only differed in their preference for a certain nearest neighbor distance, thus this trend being a pure geometrical effect, the number of atoms in the first hydration shell obtained from integrating over the first peak would remain constant. As no significant broadening of the peak would be associated with such a geometrical effect, a good measure would be a constant value of $g_{max}R_{max}^2$. In Figure 5 we show this measure versus the position of the peak. The difference in radial distribution function obtained by LDA and PBEsol, and by PBE and BLYP, lends itself to such an interpretation because no significant broadening of these peaks is seen in Figure 4. If the difference between AM05 and TPSS is also a pure geometrical effect, it is harder to determine because we do not have a direct comparison between these radial distribution functions. However, because TPSS and AM05 also give very similar dimer binding energies (see Figure 2), it is plausible that the difference is indeed purely geomerical. On the other hand, the differences between (LDA, PBEsol), (PBE, BLYP), (AM05, TPSS), and RPBE are *not* purely geometrical, and other effects must also play a role. It is, for example, evident that the RPBE peak has a significant broadening compared to the other functionals. It also appears that the differences in peak heights between TPSS and PBE, and between PBEsol and AM05,
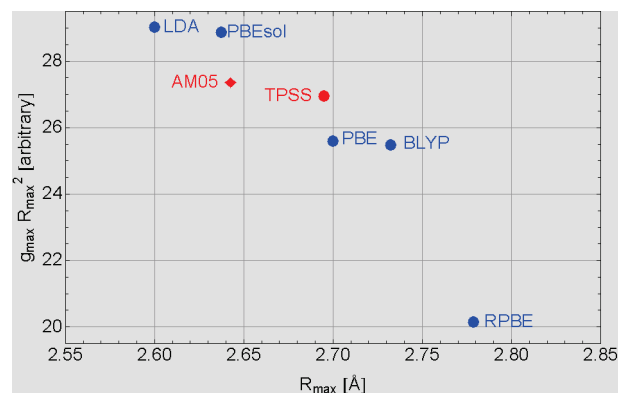
are not pure geometrical effects because they have almost the same peak position but not the same peak heights.

We can make a number of observations by comparing the results from properties of dimer binding in Table 2 with that of the structure of liquid water. For water at 300 K, AM05 and PBE yield similarly overstructured, glassy water. Interestingly, the difference in liquid water structure between RPBE and PBE is larger than the difference between AM05 and PBE.

The glassy character of water for both AM05 and PBE is intriguing because AM05 and PBE give similar, correct binding energy for the water dimer (see Table 2). RPBE behaves differently; it significantly underestimates the water dimer binding energy while it was shown by Astaghiri, Pratt, and Kress[23] to give a liquid structure at normal conditions relatively close to that of experiments.[45−48] While we confirm that RPBE yields a significantly less ordered liquid structure than that from BLYP, PBE, and AM05, the disparity in results between dimer binding energy and liquid structure for several functionals suggests that the structure of liquid water is not determined by the fundamental building block: the hydrogen bond between two water molecules.

The importance of quantum effects on liquid water has been a subject of much work in the past using empirical potentials as well as DFT, resulting in a wide range of conclusions. Although a comprehensive review of past work on this topic is significantly beyond the scope of the present work, we would like to mention that very recent large-scale DFT path-integral simulations have concluded that quantum effects reduce the structuring of liquid water[29] compared to BLYP simulations using classical hydrogens, a possibility raised by Schwegler et al.[24] as an explanation for the overstructuring of BLYP and PBE water. It has also been demonstrated that inclusion of van der Waals forces reduces the structuring compared to BLYP without dispersion corrections.[30] With quantum and van der Waals effects independently resulting in qualitative changes in structure, simulations where the hydrogen atoms are treated as classical particles performed with traditional functionals lacking well

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defined van der Waals contributions should not yield water structure in agreement with experiments at normal conditions. While quantum nuclear effects seems to only affect the peak height, inclusion of van der Waals contributions also seems to affect the first peak position. Further studies are thus needed in order to determine more accurately which of the pure functionals studied here that yields the best results if quantum nuclear and van der Waals effects are both taken into account self-consistently.

4. Summary and Discussion

Problems involving both molecules and solids remain one of the main challenges for DFT. PBE[3] is one of very few functionals extensively used for both solid and molecular systems, a strong testament to its versatility. The work of John Perdew and co-workers have thus created a framework within which a considerable range of systems can be analyzed with confidence. Directly related to confidence is a question of increasing importance: how to make quantitative estimations of the systematic uncertainties of DFT for a particular problem. This task is in practice often approached by performing calculations with multiple XC functionals. The broad use of PBE makes it an obvious functional to employ for this purpose; the remaining question is which additional functionals to include in a suite of calculations in order to gain the most information of the limitations of DFT.

The subsystem functional AM05 is based on two exact reference systems: the uniform electron gas and the surface jellium. AM05 hence constitutes a systematic improvement upon LDA by adding a description of physics derived from a surface model system to the physics derived from the uniform electron gas model system already well described by LDA. The functional's systematic improvement upon LDA has already been demonstrated for solid-state systems[7] and is established here for hydrogen bonded molecular systems by the results for the water dimer in Figure 2 and the liquid water in Figure 4. This substantial and consistent improvement over LDA supports the subsystem functional approach as a sound theoretical basis for further development. Furthermore, the AM05 functional performs as well as PBE[3] for water dimer binding energy and is slightly more structured than PBE for liquid water.

When combined with AM05's previously demonstrated high accuracy for solids,[7] these results suggest AM05 as a promising candidate to describe the physics and chemistry of solid−molecular interfaces and other mixed systems. As a functional developed on a foundation different from traditionals GGAs, AM05 brings different strenghts and weaknesses and does not follow the same trends as other functionals, as evident from Figure 2, Figure 4, and Figure 5. We suggest AM05 as a valuable additional functional to include in the analysis, in particular when experimental data is either scarce or unavailable, and it is important to estimate the systematic errors in a DFT calculation.

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