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Problems with Some Current Water Models for Close Pair Interactions That Are Not Near the Minimum Energy

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Abstract: The ability of an empirical, polarizable model of water to predict a thermal ensemble of molecular configurations at ambient conditions was examined using first-principle quantum mechanics. The empirical model of water selected for this evaluation was the TTM2-F model. The quantum mechanical methodology selected was the second-order Møller−Plesset model (MP2). Only pairwise interaction energies were considered. Significant deviations from the empirical model were found. Similar results were found for ad-hoc comparisons with several other common water models including the TIP3P, TIP4P, TIP4P-FQ, TIP5P, TTM2.1-F, TTM2.2-F, TTM3-F, and POL5/QZ potential models. Our results show that spatially close dimer configurations with interaction energies notably above the potential well minimum (but are still thermally accessible at ambient conditions) are the source of the largest deviations. To assist others in future water model parametrizations we report the MP2 near complete basis set limit energies for 840 water dimer configurations sampled from an approximate thermal ensemble at ambient conditions.

1. Introduction

This work started as an attempt to calculate the molecular radial distribution functions of bulk liquid water at room temperature using the complete basis set (CBS) limit of the second-order Møller−Plesset (MP2)[1] quantum mechanical model. Direct simulation of bulk liquid water at a density of 997 kg/m^3 requires a minimum of at least 64 water molecules to produce a simulation box large enough that system size effects can safely be ignored.[2] Direct quantum simulations using a basis set large enough to approximate the CBS limit for the MP2 model is not computationally feasible for this system size and molecular density, even using the largest supercomputers currently available. During this research the authors had hoped to circumvent this technical barrier by using non-Boltzman sampling.[3] The idea was to use a molecular dynamics simulation of an ap-

proximate water model to produce a thermal ensemble of molecular configurations and then reweight those configurations to yield the molecular distribution functions for the MP2 model. The approximate model chosen for this study was the TTM2-F model of Burnham and Xantheas.[4] This model, unlike a full MP2 quantum mechanical simulation, is relativity computationally inexpensive and allows a large number of independent molecular configurations for bulk liquid water to be generated. In order to reweight the distributions, each ensemble configuration was broken down into subsets of water dimer and trimer configurations. The two- and three-body configurational energies from each subset can then be calculated using the MP2 model near the CBS limit using a more reasonable amount of CPU resources. Each of the quantum energies is then compared directly to the energy predicted from the approximate model. The radial distribution functions for the approximate model can then be converted, through an energy reweighting process,[3] into the radial distribution for a water molecule whose interaction energies with the surrounding waters is given by a quantum

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mechanical model, while the interactions between the surrounding waters are given by the approximate model. This method avoids a large, brute force quantum mechanical simulation. This methodology has been proven successful in previous studies predicting the $g_{Na,O}$[5] and $g_{Cl,O}$[6] in high-temperature aqueous solutions. However, in the present calculations, Bootstrap error estimates showed that the 160 independent configurations sampled in this study were not nearly enough to achieve accurate radial distribution functions. Since the number of independent configurations needed is very strongly dependent on the accuracy of the model, it is easier to improve the model rather than sample thousands of configurations.

The poor result for liquid water was very surprising because the approximate model, TTM2-F, has been shown to accurately predict the MP2/CBS energies of ice clusters of 2−6 water molecules to within 0.2 kJ/mol per hydrogen bond.[4] A study of our results showed that there were many pair configurations whose interaction energies were not accurately described by the TTM2-F model. These configurations were often spatially close and far above the minimum energy configuration. Comparisons with other well-studied polarizable (TIP4P-FQ,[7] TTM2.1-F,[8] TTM3-F,[9] and POL5/QZ[10]) and nonpolarizable (TIP3P,[11,12] TIP4P,[2] and TIP5P[13]) models of water also showed poor accuracy for many of these configurations. The purpose of this paper is to report on the deficiencies of the above models. We also report all of our molecular configurations and interaction energies in the hope they will be useful in the development of new and more accurate water models.

2. Methods

Molecular trajectories from a NVT simulation for a system of 128 TTM2-F water molecules at room temperature were provided by George Fanourgakis and Sotiris S. Xantheas. From these configurations 160 independent configurations were sampled. To efficiently calculate ΔU for each configuration it is convenient to explicitly define the total potential energy for each configuration, U, as a series of single- and multiple-body interactions

$$U = \sum_i u_i^o + \sum_i (u_i - u_i^o) + \sum_{i<j} (u_{ij} - u_i - u_j) + \sum_{i<j<m} (u_{ijm} - u_{ij} - u_{im} - u_{jm}) + \dots \quad (1)$$

where $u_{\{x\}}$ denotes the total potential energy contained in a set of $\{x\}$ molecules and the first, second, third, and fourth terms denote the minimum potential energy of the monomers, the distortion energy of the monomers, the pair wise potential energies (U_2), and the three-body potential energies (U_3), respectively. In this study we calculated only the pairwise potential energies, U_2.

Pairwise potential energies (U_2) were calculated using MP2/aug-cc-pVDZ (U_{DZ}) and MP2/aug-cc-pVTZ (U_{TZ}) quantum methods. All quantum calculations were performed using the NWChem software package (version 4.7).[14] For all MP2 calculations basis set superposition error (BSSE) corrections were made using the counterpoise method.[15]

Preliminary comparisons of the DZ energies with the TTM2 model showed many large differences for oxygen−oxygen distances (R_{OO}) less than 4.1 Å. We selected 60 dimer outliers from the first solvation shell ($R_{OO} < 4.1$) and performed additional MP2/aug-cc-pVQZ (U_{QZ}) and MP2/aug-cc-pV5Z (U_{5Z}) calculations (corrected for BSSE). We repeated these calculations using 50 additional dimer geometries chosen at random again with $R_{OO} < 4.1$ Å. The complete basis set limit for pairwise interactions (U_{CBS}) for each configuration was determined by fitting the following equation

$$U_{LZ} = U_{CBS} + \frac{b}{(1 + L)^4} + \frac{c}{(1 + L)^5} \quad (2)$$

where U_{CBS}, b, and c are adjustable parameters. The value L denotes the maximum angular momentum for the aug-cc-pVDZ, aug-cc-pVTZ, aug-cc-pVQZ, and aug-cc-pV5Z basis sets and was taken to be 2, 3, 4, and 5, respectively. Energies that were not BSSE corrected did not typically show a clear convergence progression with increased basis set size, so they were not used.

We noticed a strong correlation of both R_{OO} and ($U_{TZ} - U_{DZ}$) with ($U_{TZ} - U_{CBS}$) for our sample of 110 pair configurations. Least-squares fits showed that U_{TZ} could be corrected to near the CBS limit (NCBS) by the equation

$$U_{NCBS} = U_{TZ} + 0.238 + 0.280(U_{TZ} - U_{DZ}) + \\ 0.0263(U_{TZ} - U_{DZ})^2 - 148.9 R_{OO}^{-5} \quad (3)$$

where the energies are given in units of kJ/mol and the distances are in units of Angstroms. For our sample of 110 pair configurations, U_{NCBS} is more accurate than U_{5Z}: the average and standard deviation of ($U_{CBS} - U_{NCBS}$) are 0.00 and 0.13 kJ/mol, respectively, while for ($U_{CBS} - U_{5Z}$) they are −0.245 and 0.13 kJ/mol. The maximum difference between U_{CBS} and U_{NCBS} was 0.34 kJ/mol. This correlation appeared highly accurate, so we used it to calculate U_{NCBS} for all of our 840 pair configurations with $R_{OO} < 4.1$ Å.

During the course of this research it also became clear that an unphysical decrease in the van der Waals potential of the TTM2-F model at O−O distances of under 2.2 Å could cause unrealistic molecular configurations to be generated during a molecular dynamics simulation run. A revised form of the TTM2-F dubbed TTM2.1-F with the addition of an extra exponential repulsive term was published to correct this problem.[8] As a precaution we checked all the oxygen−oxygen distances inside our selected clusters and found that only a few were under 2.5 Å and none were under 2.4 Å. The difference in the van der Waals potential energy between the TTM2-F and TTM2.1-F potential models at the energy minimum for $R_{OO} = 2.4$ and 2.5 Å is 0.7 and 0.2 kJ/mol, respectively, giving us confidence that this deficiency in the TTM2-F model did not significantly skew our sampling of the ensemble. We then calculated the energies of the TTM2.1-F model using the same configurations selected from the TTM2-F ensemble. The results were very similar, and the energy differences between the TTM2.1-F and the MP2/CBS models remained quite large.
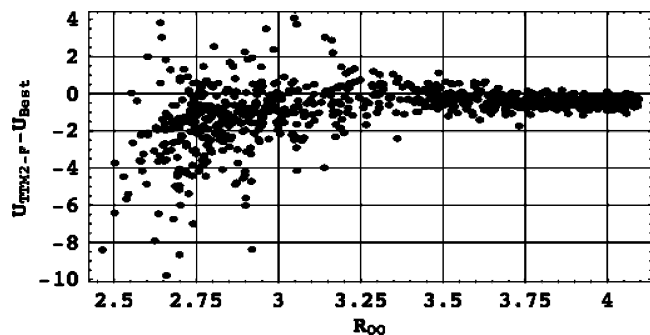
Figure 1. Differences in pairwise energy between the TTM2-F model and the Best MP2 estimate ($U_{\text{TTM2-F}} - U_{\text{Best}}$) are plotted versus R_{OO} (Å) for our sample of 840 pairs. U_{Best} is the near CBS limit when the CBS limit is not available. Energies are given in kJ/mol.
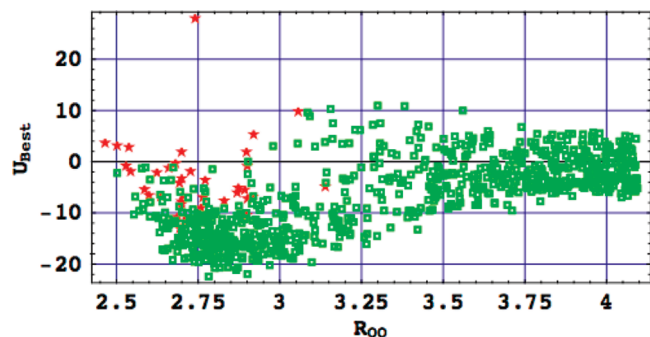

Figure 2. Pairwise energies for the interaction of a central water molecule with another surrounding water molecule, U_{Best}, as a function of the oxygen−oxygen distance, R_{OO} (Å). The 5% of points with the largest errors ($U_{\text{TTM2-F}} - U_{\text{Best}}$) are plotted as red stars. These 42 points have model energies, $U_{\text{TTM2-F}}$, that are too negative by −3.8 to −9.9 kJ/mol. Energies are given in kJ/mol.

3. Results and Discussions

3.1. Comparison with the TTMX-F Models. We then compared the models with our most accurate pairwise energy, U_{Best}, which was U_{NCBS} when U_{CBS} was not available. Please note that we calculated $u_{ij} - u_i - u_j$ for both models, and this did not include the distortion energy, $u_i - u_o$ energy.

Figure 1 shows the difference $U_{\text{TTM2-F}} - U_{\text{Best}}$ as a function of R_{OO}. For R_{OO} greater than 3.2 Å the differences are small. For R_{OO} less than 3.2 Å, the energy differences are much larger and ranged from +4 to −10 kJ/mol, with an average difference of −0.8 kJ/mol and a standard deviation of 1.5 kJ/mol. For our sample of 840 pairs with $R_{\text{OO}} < 4.1$ Å there are a few outliers that are too high in energy by 2−4 kJ/mol and many outliers that were too low in energy by 4−10 kJ/mol. Figure 2 shows U_{Best} versus R_{OO} for all water dimers with $R_{\text{OO}} < 4.1$. There are many near-neighbor water molecules possessing repulsive pairwise interactions that are up to 12 kJ/mol and even one as high as 28 kJ/mol. In Figure 2 the 5% of points with the largest errors are plotted as red stars. These 42 points have TTM2-F model energies that are too negative by −3.8 to −9.9 kJ/mol. Figure 2 shows that these outliers occur when R_{OO} is short and U_{Best} is high, that is, these molecules are close neighbors but do not form strong hydrogen bonds. The TTM2-F model does not reflect these
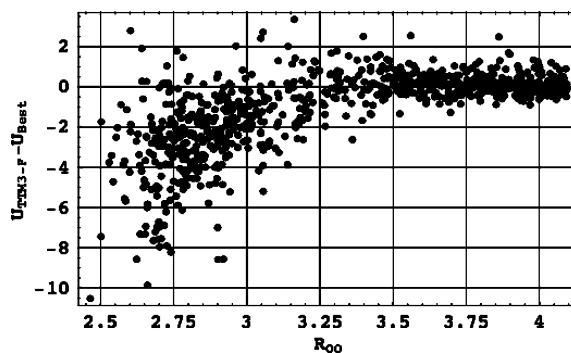

Figure 3. Differences in the pairwise energy between the TTM3-F model and the Best MP2 estimate ($U_{\text{TTM3-F}} - U_{\text{Best}}$) are plotted versus R_{OO} for our sample of 840 pairs. U_{Best} is the near CBS limit when the CBS limit is not available. Energies are given in kJ/mol.
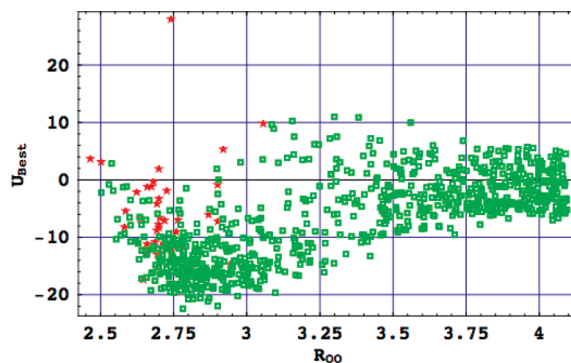

Figure 4. Pairwise energies for the interaction of a central water molecule with another surrounding water molecule, U_{Best}, as a function of the oxygen−oxygen distance, R_{OO}. The 5% of points with the largest errors ($U_{\text{TTM3-F}} - U_{\text{Best}}$) are plotted as red stars. These 42 points have model energies, $U_{\text{TTM3-F}}$, that are too negative by −4.9 to −10.2 kJ/mol. Energies are given in kJ/mol.

ab initio predictions and instead describes dimer energies that are considerably lower. We suppose the source of these discrepancies could be either (1) an unknown deficiency in the equations governing the potential model or (2) a failure to appropriately represent these kinds of configurations during parametrization.

Next we considered the TTM3-F model,[9] which is a substantial revision motivated by the failure of this and other models to reproduce the OH stretching vibrations in both water clusters and in liquid water. Using the same configurations selected from the TTM2-F ensemble the dimer energies were recalculated using the TTM3-F potential model. For our selected configurations with $R_{\text{OO}} < 4.1$ average differences between the TTM2-F and the TTM3-F models were small. The average difference is −0.23 kJ/mol, with a maximum positive difference of 2.5 kJ/mol and a maximum negative difference of −5.3 kJ/mol. Although Figures 3 and 4 show that the revisions from the TTM2-F model to the TTM3-F model did increase the number of outliers below −6 kJ/mol from 11 to 22, the 11 configurations that were the worst outliers for the TTM2-F model are still outliers in the TTM3-F model (<−6 kJ/mol) and the outliers again occur mainly for interactions between very close neighbors. Of the 22 outliers, 20 have configurations that would normally be

called hydrogen bonds ($R_{OO} < 3.2$ Å and O−H−O angle > 140°). The hydrogen bond length is also very short (1.46 < R_{OH} < 1.82) for 17 of the 20 configurations. The other two outliers have R_{OH} near 2 Å and O−H−O angles near 127°. These findings indicate there are many configurations that are both accessible at ambient temperatures and not well represented by either the TTM2-F or the TTM3-F model.

In addition to the outliers, there is a systematic bias in the results; the average differences are $U_{TTM-F} - U_{Best}$, −0.8 kJ/mol, and $U_{TTM3-F} - U_{Best}$, −1.1 kJ/mol. The systematic bias in the dimer energies is cumulative and leads to significant errors for the entire molecular configuration. Since these models have the correct total energy for liquid water at ambient conditions, a systematic and canceling error in the multibody interactions is possible.

3.2. Comparison with Other Models. The poor performance of the TTM2-F and TTM3-F models surprised us, so we looked at some of the standard water models to see how they performed. To this end we arbitrarily chose the TIP3P, TIP4P, TIP4P-FQ, TIP5P, and POL5/QZ models and calculated the energy for the 110 configurations for which we had MP2/CBS energies. The TIP3P (its simplest flexible form was used[12]) and TIP4P models were studied because of their prevalence in commercial molecular dynamics simulations. The TIP5P model was included because of its excellent description of g_{OO} as measured by recent X-ray diffraction experiments.[13] Technically it is not fair to compare the TTM2-F dimer configurations using water potentials with a fixed internal geometry. Complete fairness however was not our purpose here as we only wanted to gain a generalized understanding as to how well other models performed for these configurations, and we settled on making an ad-hoc comparison with two slightly different methods. In one comparison, the rigid model was confined to the plane of the flexible model with oxygens superimposed and the M site on the H−O−H bisector (the A models). In the other comparison the rigid molecules were distorted with oxygens and hydrogens superimposed, and the M site was positioned on the bisector. To calculate the energy of this distorted configuration the site−site interactions between the water molecules were calculated with the usual algorithm even though the molecule was distorted (the B models). The differences between the two calculations (A and B) were small compared to the errors discussed here (see below).

We first examined the distribution of energy differences between the models. Figure 5 shows the percentile distribution of energy differences between each model and the ab initio pairwise energies ($U_{Model} - U_{CBS}$). The small uncertainties shown in Figure 5 were estimated from the difference between the results of the two methods of calculation (A and B above).

As expected, the TTM2-F and TTM3-F models were very similar and the most accurate. They have the smallest spreads of any models with a fairly negative bias. The polarizable TIP4P-FQ and POL5/QZ models show a smaller but positive bias, but the spreads are larger. Both of these models had smaller minimum errors than the TTM3-F model (the minimum errors are only about −4 kJ/mol). However, these
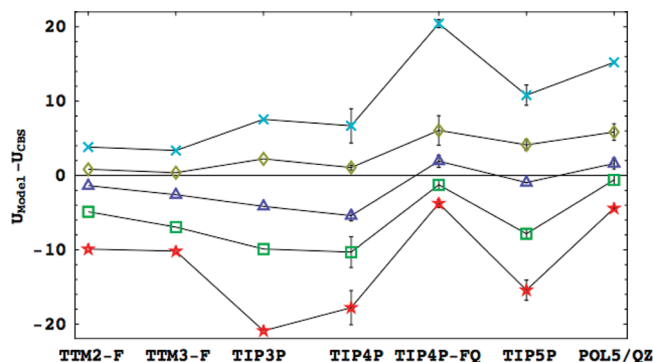

Figure 5. Percentile distributions of the differences in pairwise energy ($U_{Model} - U_{CBS}$) for 110 configurations are plotted for each model. The symbols are from top to bottom: the maximum difference, the difference that is higher than 83.5% of the differences, the median difference, the difference that is higher than 16.5% of the differences, and the minimum difference. Energies are given in kJ/mol. Uncertainties less than the symbol size are not shown.

models had much higher maximum errors (the maximum energies are 15 and 20 kJ/mol, respectively).

It is important to note that comparing the present ab initio pairwise energies to nonpolarizeable models, such as the TIP3P, TIP4P, and TIP5P models, is also not fair because these models were never meant to reproduce specific pairwise interactions. They instead use an "effective" pair interaction that was empirically adjusted to compensate for the average multibody interactions in liquid water at room temperature. This compensation is probably the reason for the negative biases of these models. The TIP5P model however, which is known to give an excellent description of the oxygen−oxygen radial distribution function at ambient conditions, appears to have a minimal average bias in the pairwise interactions. This is puzzling because we would expect a more negative bias because the effective pairwise potential should include a significant contribution to empirically account for attractive three-body interactions. In our opinion these three models have some very large errors that are too large to be solely due to neglecting compensations for multibody effects. As before, the largest errors were spatially close.

For each model we plotted both the error and U_{Best} as a function of R_{OO} as in Figures 1 and 2 to find out where the largest outliers were located. We looked at the top 11 outliers of each model. For all models the A and B comparisons were very similar. The highest 11 outliers all had R_{OO} less than 3 Å with most of them being close interactions with R_{OO} less than 2.75 Å. For TTM3-F, TIP3P, and TIP4P (A and B) the top 11 outliers were all negative and TIP5P had most of its outliers negative. For TIP4P-FQ and POL5/QZ the outliers were all positive. This is interesting as the TIP4P-FQ and POL5/QZ are fluctuating point charge models and treat polarization in a fundamentally different way than the TTM2-F and TTM3-F models. The values of U_{Best} showed that almost all of the outliers did not have strong hydrogen bonds. We also checked whether the same configurations tended to be outliers for more than one model. We found that only 12 configurations accounted for 59% of the outliers

for the models in Figure 5. Nine of these 12 configurations had large errors with both polarizable and nonpolarizable models.

4. Concluding Remarks

Many current models do a poor job of representing spatially close dimer interactions that are not near the minimum energy. There are substantial numbers of these "outliers" found in simulations of water at ambient conditions, so adjustments to the models are necessary. It is believed that ab initio methods are very helpful in parametrizing polarizable models for close interactions. Complete results on the 840 pairs used in this study are given in the Supporting Information, so that these pairs can be used in future modeling efforts. The main limitation of this study is that only pairwise interactions were studied. The errors found are much larger than the expected errors in the quantum method used.

Supporting Information Available: Complete results including coordinates and energies of the 840 pairs used in this study. This material is available free of charge via the Internet at http://pubs.acs.org.

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