Quantum Chemical Tests of Water-Water Potential for Interaction Site Water Models

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Dedicated to Prof. Dr. Gorazd Vesnaver on the occasion of his 70th birthday

Abstract

Accuracy of different simple interaction site water models was tested. Instead of assessing their quality through the calculations of various water physical properties (dipole moment, dielectric constant, phase-equilibria diagrams, etc.) and comparison with experimental values, we calculated water-water potential and compared it with the potential from quantum chemical calculations.

Using density functional theory (DFT) water-water potential was calculated for different positions of two water molecules, which was compared with the interaction used in water models. Different simple interaction site water models were then evaluated and assessed. Special emphasis is placed on angle and distance dependence of water-water potential around minima in the potential. Among three-, four-and five-site electrostatic water models, TIP3P, TIP4P/2005 and TIP5P were found to be the most accurate.

Keywords: Hydrogen bonds, local field, quantum chemistry

1. Introduction

Water is one of the most abundant compounds on Earth and undoubtedly the most important one. It has crucial applications in industry, transportation and has played a vital role for the development of life. Additionally, water is known to exhibit many unusual phenomena, such as density maximum at 4 °C and negative coefficient of thermal expansion below that temperature, high heat capacity, surface tension and viscosity,[1] which are ascribed to the formation of hydrogen bonds. Because of this overwhelming importance of water molecule and its peculiarities, numerous attempts at describing the water molecule and simulating bulk properties of water[2–8] and its behaviour[9–20] have been made. With the advent of computers in the 20th century, simulating bulk properties and behaviour of water and aqueous solutions has become a feasible task.

Quantum-mechanical theories in principle allow for exact calculations, but the available computing power has been the bottle-neck that has so far limited their use to systems consisting of no more than a few molecules.[21] As a consequence, there has been a persistent need to develop various simplified water models that seek a compromise between accuracy and computational cost. Dozens of water models have been proposed, ranging in complexity from simple three-point interaction site models to complex polarisable models.

Water models can be grouped into three types. Simple interaction site models, which are the focus of this paper, describe the water model as a rigid constellation of charged and non-charged spherical particles that interact according to Lennard-Jones potential and Coulomb law. Their spin-off are flexible models,[22–26] which introduce non-rigid structure by using harmonic angle bending for the HOH angle or bond stretching for the OH bonds. Allowing for polarisation effects and many-body effects yields polarisable models[27–39] that have a considerably larger computational cost. Since computational efficiency is an important factor in system with large number of molecules, simple water models using effective pairwise potentials with no explicit polarisation and many-body effects are usually used.[40] Water models including those effects are thus beyond the scope of this paper. Lastly, primitive models like Nezbeda's water models[41] and Mercedes-

Benz water models[42–48] represent water as hard or Lennard-Jones spheres that interact through short range potential and association type of potential, which mimics the formation of hydrogen bonds.

Simple interaction site models can be further divided into three-, four-, five-and lately also six-site models.[49] Parameters for a particular model (such as bond length, angle size, charge size, Lennard-Jones parameters) are usually chosen after running molecular dynamics or Monte Carlo simulations so as to ensure the best reproduction of an arbitrarily chosen bulk property. Normally, the model geometry would be very close to the actual geometry of water molecule.

In this paper, we try to assess the quality of the most popular simple site interaction water models in a different way than found in literature. If a model is to realistically depict behaviour and bulk properties of water, it is reasonable to expect an accurate description of water-water potential on a molecular scale. Instead of the conventional method that consists of running molecular simulations to extract a particular bulk property, we compare the models' predictions for water-water interaction potential in vacuum with exact quantum calculations for various distances and orientations.

2. Methods

Quantum chemical calculations were performed with standard density functional theory (DFT) using the Gaussian 09 program suite,[50] employing B3LYP density functional (DFT) method with 631++G(df) basis set.[51] The B3LYP functional is a linear combination of Hartree-Fock exchange,[52,53] 1988 Becke exchange[54,55] and LYP correlation.[56] Water geometries optimisation showed the results to be relatively invariant to the method or basis set used. For instance, water geometry optimisation using B3LYP, CCSD[57–60] and MP2[61] chemistries with the aug-cc-pVTZ[62,63] basis set yields very similar geometries (bond lengths 0.960, 0.959, and 0.961 Å; angles 105.2°, 104.5°, and 104.1°, respectively). B3LYP/6-31++G(df) was ultimately chosen as the best compromise between the computational cost and the accuracy of the results.

Geometry of the water molecule was constructed to match the experimental data (OH bond length 0.9572 Å, HOH angle 104.52°)[64] for an isolated water molecule in a vacuum and then kept constant in all configurations which is equivalent to how simple models of water treat interaction. Electronic energies are reported in a relative respect with energy of two isolated water molecules at the infinite distance being set to zero. Water-water potential for three-point interaction site water models SPC,[65] TIP3P,[66] TIPS,[67] four-point interaction site models BF,[68] TIP4P,[69] TIP4P-Ew,[70] TIP4P/Ice,[71] TIP4P/2005[72] and five-point interaction site models, TIP5P,[73] TIP5P-E[74] was calculated using the geometry of the water molecule as prescribed by

the model. In these models, van der Waals interactions are approximated with Lennard-Jones potential between the spheres, centred on the oxygen atoms, while hydrogen bonds are approximated implicitly through Coulomb interaction between the charged sites. The total interaction calculated as the sum of the two contributions is compared with the electronic energies from DFT method for different distances and relative positions of two water molecules in vacuum. The quality of a model is determined by the agreement of the model prediction for interaction strength with the DFT energies.

3. Results and Discussion

3. 1. Distance Dependence

Two water molecules were placed in a tetrahedral orientation that is particularly favourable for the formation of hydrogen bond. Atoms of the first molecule are labelled as H^{1a}, H^{1b}, and O^1 and those of the second molecule as H^{2a}, H^{2b}, and O^2. The orientation can be described as having atoms $O1$, H^{1a}, and O^2 on a straight line that forms the angle of 125.24° with the bisector of the angle $< H^{2a}O^2H^{2b}$ (see figure 1).
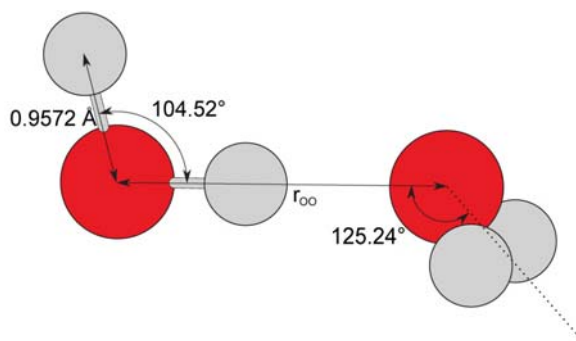

Figure 1: Geometry of two water molecules when distance between oxygen atoms r_{OO} is varied from 2.3 to 5.0 Å.

Interaction strength was calculated for the oxygen-oxygen distances r_{OO} between 2.3 Å and 5.0 Å with the step size $\Delta r = 0.001$ Å and compared with the potential of three-point interaction site models (see figure 2), four-point interaction site models (see figure 3) and five-point interaction site models (see figure 4). For each model, the maximum predicted interaction strength and the corresponding oxygen-oxygen distance were computed and compared with the obtained values 2.892 Å and 6.149 kcal mol^{-1} from quantum computation. Additionally, we calculated the average discrepancy between the model prediction and quantum calculation (see table 1) as

$$\sqrt{\overline{(\Delta E)^2}} = \sqrt{\frac{1}{N+1} \sum_{i=0}^{N} \left(E_{\text{model}}(r + i\Delta r) - E_{\text{quantum}}(r + i\Delta r) \right)^2} \quad (1)$$

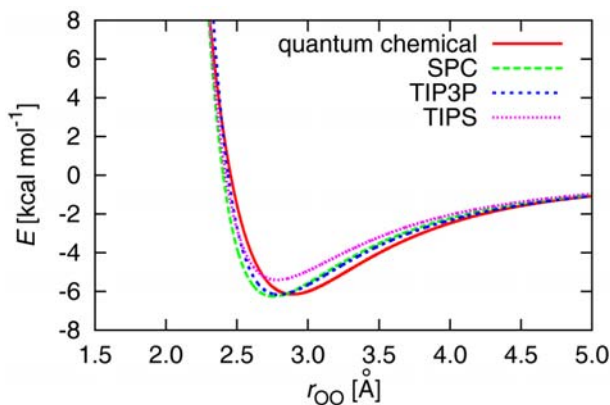with $r = 2.3$ Å, $\Delta r = 0.001$ Å and $N = 2700$.

Figure 2: Distance dependence of interaction strength for three-point interaction site water models in orientation showed in figure 1. Solid: quantum chemical; long dashed: SPC; dashed: TIP3P; dotted: TIPS.
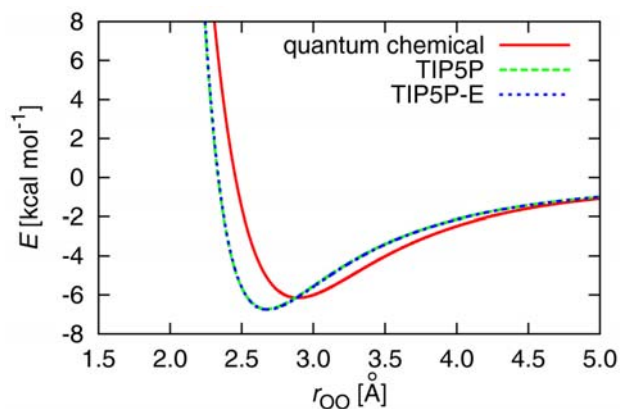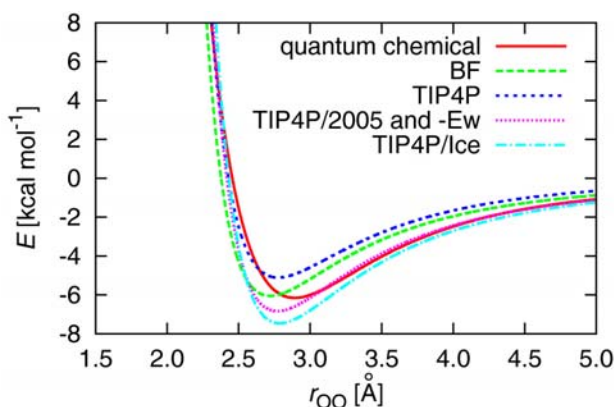

Figure 3: Same as figure 2 only for four-point interaction site water models. Solid: quantum chemical; long dashed: BF; dashed: TIP4P; dot-dashed: TIP4P/Ice; dotted: TIP4P/2005 and TIP4P-Ew.

Table 1: Comparison of the average discrepancies between the model prediction and quantum calculation for interaction strength $\sqrt{\overline{(\Delta E)^2}}$. Water models also predict different maximum interaction strength E_{max} and the corresponding oxygen-oxygen distance r_{OO}.

Model	$\sqrt{\overline{(\Delta E)^2}}$ [kcal mol^{-1}]	r_{OO} [Å]	E_{max} [kcal mol^{-1}]
SPC	1.424	2.757	6.256
TIP3P	0.885	2.751	6.162
TIPS	0.703	2.783	5.403
BF	1.224	2.727	6.049
TIP4P	0.954	2.778	5.102
TIP4P-Ew	0.929	2.751	6.783
TIP4P/Ice	0.954	2.790	7.455
TIP4P/2005	0.728	2.773	6.834
TIP5P	1.682	2.676	6.752
TIP5P-E	1.719	2.751	6.783
quantum chemical	N/A	2.892	6.149

Figure 4: Same as figure 2 only for five-point interaction site water models. Solid: quantum chemical; long dashed: TIP5P; dashed: TIP5P-E.

Among the three-point interaction site models, TIP3P and TIPS do comparatively well in describing the interaction strength across the whole range of oxygen-oxygen distances. However, TIPS predicts a very shallow interaction well compared to quantum results. This is reflected in recent research, where TIP3P is almost universally used among the three-point models.

BF is one of the oldest water models at all, having been proposed by Bernal and Fowler in 1933. Due to its venerable age, BF does its job worse than modern TIP4P models and is nowadays only of historical interest. Among the latter, TIP4P/2005 exhibits the smallest discrepancy between its predictions for interaction strength and quantum calculations, also reflected in its leading share among four-point models in recent research. It is worth nothing that the TIP4P/Ice model predicts by far the strongest interaction strength of 7.455 kcal mol^{-1}. This is because the model is optimised for describing the solid phase of water where hydrogen bonds are stronger than in liquid phase.

Differences between both examined five-point interaction site models are neglible. This is expected behaviour since models are parametrised almost identically with very minor differences in Lennard-Jones parameters (σ: 3.120 and 3.097 Å, ε: 0.1600 and 0.1780 kcal mol^{-1}, respectively).

While there is some variation among the predicted interaction strength, all models invariably predict the corresponding oxygen-oxygen distance too short. In vacuum, the distance between two water molecules is greater than in liquid phase. Since models were primarily designed to describe the liquid phase, they must take this phenomenon into account. Our quantum calculation was, however, done for a dimer in vacuum, explaining the difference in interaction distance.

3. 2. Angle Dependence

To investigate the angle dependence, the same atom labels were retained. Two water molecules are then orien-

ted as follows: atoms O^1, H^{1a}, and O^2 shall be placed on a straight line. The atom H^{1b} shall lie in the same plane, which is also the bisector of the angle $< H^{2a}O^2H^{2b}$. Angle ϕ is defined with one ray through H^{1a} and O^2, the other ray being the bisector of the angle $< H^{2a}O^2H^{2b}$ and the vertex being the atom O^2 (see figure 5). The oxygen-oxygen distance shall be fixed at 2.892 Å. The angle was varied from 0° to 360° with the step size $\Delta\phi = 0.1°$.
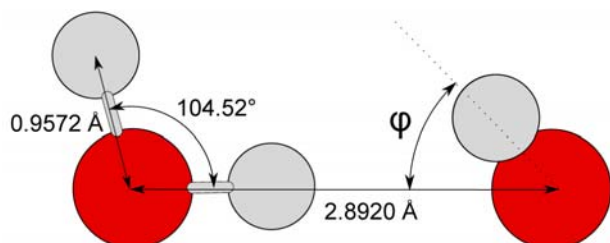

Figure 5: Geometry of two water molecules when orientation of the second molecule ϕ is varied from 0 to 360°.

The other orientation for investigating the angle dependence is set as follows. Atoms O^1, H^{1a}, H^{1b} and O^2 shall lie in one plane. The line between the atoms O^1 and O^2 shall be the bisector of the angle $< H^{2a}O^2H^{2b}$. Angle θ is defined with the vertex O^1 and one ray going through H^{1a} and the other ray going through O^2 (see figure 6). The oxygen-oxygen distance remains fixed at 2.892 Å. The angle was varied from 0° to 360° with the step size $\Delta\theta = 0.1°$.

Interaction strength was calculated for the whole range values for angles ϕ and θ (see figures 7, 8, 9, 10, 11, 12). Again, average discrepancies between the model prediction and quantum calculation $\sqrt{(\Delta E_\phi)^2}$ and $\sqrt{(\Delta E_\theta)^2}$ are calculated and compared among the models (see table 2).

$$\sqrt{\overline{(\Delta E_\alpha)^2}} = \sqrt{\frac{1}{N+1}\sum_{i=0}^{N}\left(E_{\text{model}}(\alpha + i\Delta\alpha) - E_{\text{quantum}}(\alpha + i\Delta\alpha)\right)^2} \quad (2)$$
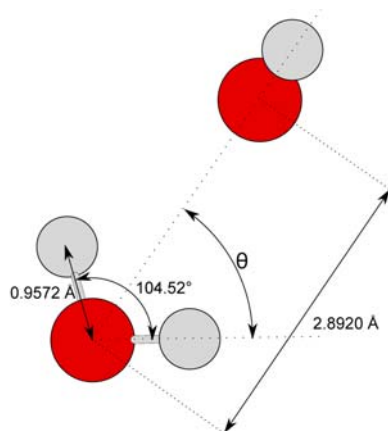
with $\alpha = 0°$, $\Delta\alpha = 0.1°$ and $N = 3600$.

Figure 6: Geometry of two water molecules when orientation of the first molecule θ is varied from 0 to 360°.
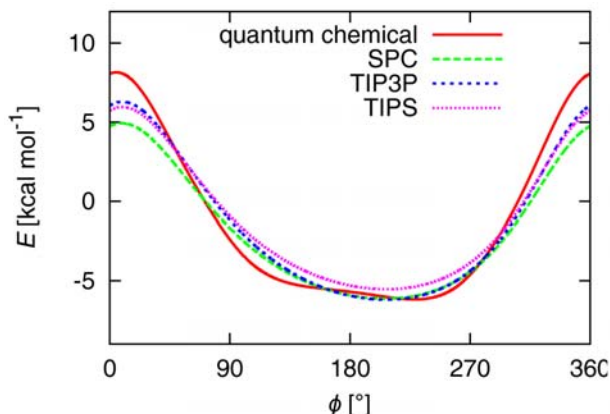

Figure 7: Angle ϕ dependence of interaction strength for three-point interaction site water models. Solid: quantum chemical; long dashed: SPC; dashed: TIP3P; dotted: TIPS.
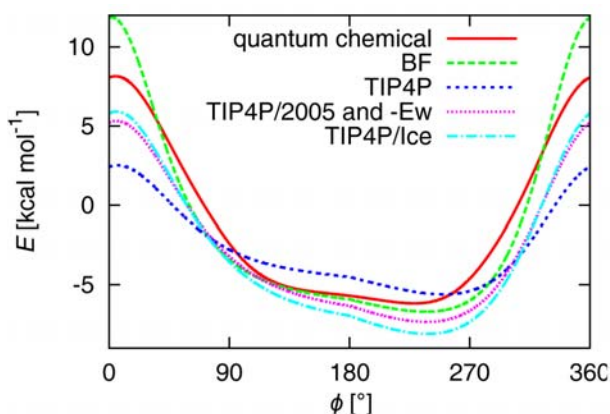

Figure 8: Same as figure 7 only for four-point interaction site water models. Solid: quantum chemical; long dashed: BF; dashed: TIP4P; dot-dashed: TIP4P/Ice; dotted: TIP4P/2005 and TIP4P-Ew.
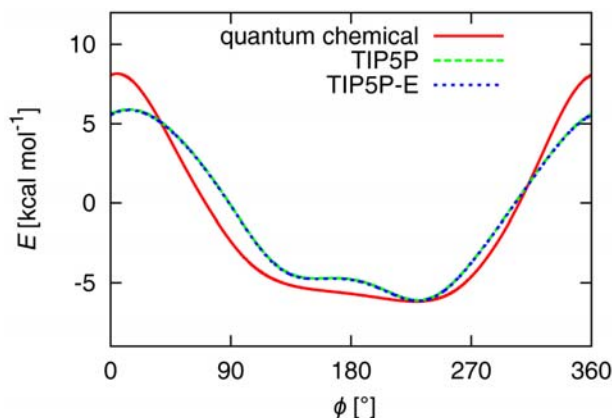

Figure 9: Same as figure 7 only for five-point interaction site water models. Solid: quantum chemical; long dashed: TIP5P; dashed: TIP5P-E.
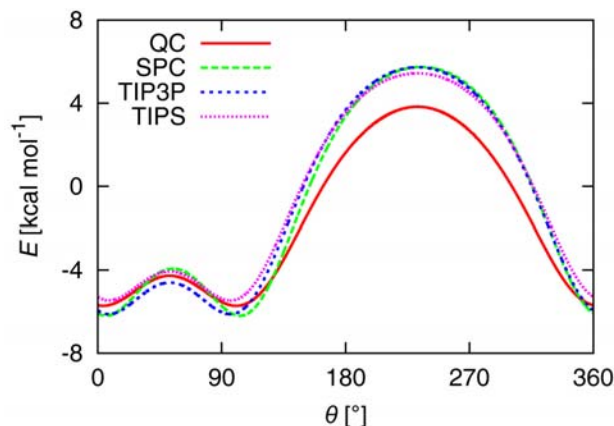
Figure 10: Angle θ dependence of interaction strength for three-point interaction site water models. Solid: quantum chemical; long dashed: SPC; dashed: TIP3P; dotted: TIPS.
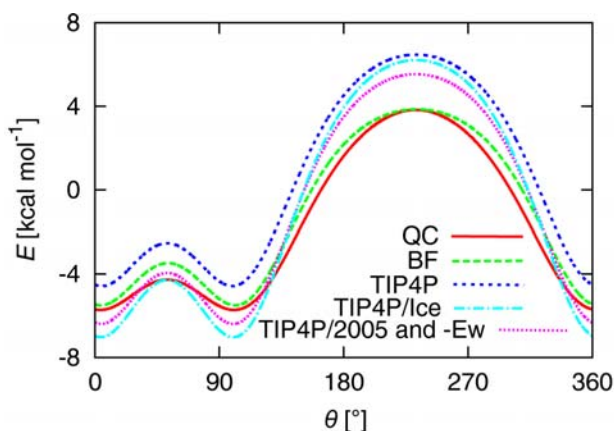
Table 2: Comparison of the average discrepancies between the model prediction and quantum calculation for interaction strength $\sqrt{E_\phi^2}$ and $\sqrt{(E_\theta)^2}$.

Model	$\sqrt{\overline{\Delta E_\phi^2}}$ [kcal mol^{-1}]	$\sqrt{\overline{(\Delta E_\theta)^2}}$ [kcal mol^{-1}]
SPC	1.424	1.368
TIP3P	0.960	1.443
TIPS	1.199	1.406
BF	1.424	0.571
TIP4P	2.868	2.278
TIP4P-Ew	1.619	1.286
TIP4P/Ice	2.108	1.650
TIP4P/2005	1.952	1.274
TIP5P	1.293	1.136
TIP5P-E	1.280	1.123

TIP3P model once again stands out as the best three-point interaction site model, followed by the TIPS. As with the distance dependence comparison, SPC model performs poorly, further warranting the prevailing use of TIP3P in recent simulations.

As for the four-point models, BF curiously seems to perform exceedingly well in one conformation (when varying θ, see figure 11). However, this does not suffice to ascribe high accuracy to this model due to its poor performance in the other configuration. The most consistent four-point models are TIP4P-Ew and TIP4P/2005. Again, TIP4P/Ice is penalised due to its prediction of very strong ice-like interactions. Predictions from TIP5P and TIP5P-E models again almost coincide due to similar parametrisation.

Figure 11: Same as figure 10 only for four-point interaction site water models. Solid: quantum chemical; long dashed: BF; dashed: TIP4P; dot-dashed: TIP4P/Ice; dotted: TIP4P/2005 and TIP4P-Ew.
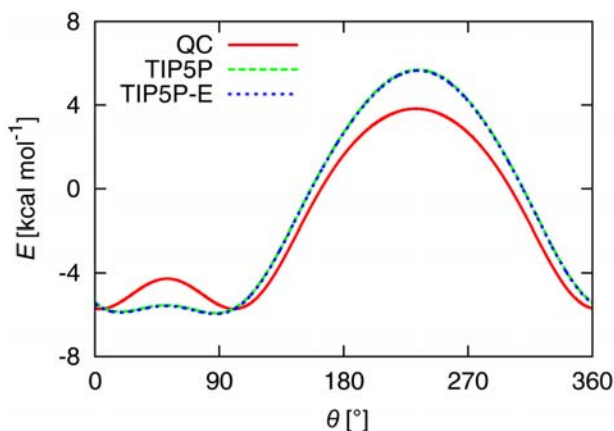
4. Conclusion

Tables 1 and 2 summarise the comparison of water models with quantum calculations. This data points to the conclusion, that the most accurate water models on a molecular scale are TIP3P for three-site models, TIP4P/2005 for four-site models, while there is no significant difference between TIP5P and TIP5P-E models. Comparison across different model families would be difficult because of very different structure and parameters they use.

One must take caution when interpreting this data. Water models discussed here have been devised for the description of condensed water phases, while our comparison focuses on the vacuum-like environment. Since models use only pair-wise potential, ternary and higher potentials are averaged out and included implicitly through slightly corrected *effective* pair-wise potential. When describing a water dimer in vacuum, there are no higher potentials to be accounted for.

However, our data is still in excellent agreement with literature data on calculated macroscopic properties of water from different models (see table 3). Three-site models use too few variables and consequently fail to ac-

Figure 12: Same as figure 10 only for five-point interaction site water models. Solid: quantum chemical; long dashed: TIP5P; dashed: TIP5P-E.

curately reproduce macroscopic properties, such as freezing point or density maximum. Four-site water models are plagued by a very poor estimate for dielectric constant but on the other hand do remarkably well in predicting density maximum. Among them, TIP4P/2005 is superior on the macroscopic and molecular scale. Five-site models TIP5P and TIP5P-E are almost indistinguishable on a molecular scale. However, even small differences in parametrisation result in noticeable deviations in macroscopic properties predictions. TIP5P gives much better estimates for freezing point and density maximum.

Table 3: Physical properties of liquid water at 25 °C and 1 atm as predicted by water models.[78]

model	dipole moment [D]	dielectric constant	freezing point for I_h ice [°C]	density maximum [°C]
SPC	2,27	65	–83[75]	–45
TIP3P	2,35	82	–127[75]	–91
TIP4P	2,18	53	–41[75]	–25
TIP4P-Ew	2,32	62,9	–28[75]	+1
TIP4P/2005	2,305	60	–21[71]	+5
TIP5P	2,29	81,5	1[75]	+4
TIP5P-E	2,29	92	–2[76]	+8
experimental	2,95	78,4	0,0025[77]	+3,984

Our results confirm the notion that water models should be accurate already on a molecular scale if we hope to get useful results for macroscopic properties and behaviour in simulations. In this way, initial parameters for new models or reparametrisation of the existing ones can be deduced from quantum chemical calcuations and then refined via molecular simulations.

5. Acknowledgement

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Povzetek

Preverili smo natančnih enostavnih modelov vode. Namesto da bi njihovo kakovost ocenili na podlagi izračuna več fizikalnih lastnosti vode (dipolni moment, dielektrična večna konstanta, fazni diagrami itd.) in njihove primerjave z eksperimentalnimi vrednostmi, smo izračunali potencial, ki deluje med molekulama vode, in ga primerjali s potencialom, ki smo ga izračunali s kvantnimi metodami.

Z uporabo teorije gostotnega funkcionala (DFT) smo izračunali potencial med molekulama vode v različnih položajih, ki smo ga nato primerjali z napovedmi modelov. Na ta način ocenili njihovo kakovost. Še poseben poudarek je na odvisnosti potenciala od medsebojne razdalje med molekulama in na kotni odvisnosti v bližini minimumov. Ugotovili smo, da so med tri-, štiri-in pettočni modeli TIP3P, TIP4P/2005 in točkovnimi modeli vode najbolj natančni TIP5P.