Quantum Dynamics of Water from Møller-Plesset Perturbation Theory via a Neural Network Potential

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Abstract: We report the static and dynamical properties of liquid water at the level of second-order Møller-Plesset perturbation theory (MP2) with classical and quantum nuclear dynamics using a neural network potential. We examined the temperature-dependent radial distribution functions, diffusion, and vibrational dynamics. MP2 theory predicts over-structured liquid water as well as a lower diffusion coefficient at ambient conditions compared to experiments, which may be attributed to the incomplete basis set. A better agreement with experimental structural properties and the diffusion constant are observed at an elevated temperature of 340 K from our simulations. Although the high-level electronic structure calculations are expensive, training a neural network potential requires only a few thousand frames. This approach shows great potential, requiring modest human effort, and is straightforwardly extensible to other simple liquids.

1. Introduction

Water, a prerequisite for our existence on this planet, plays a vital role in nearly all environmental, biochemical, physical processes, whether in bulk or at interfaces [1,2]. Water's anomalous properties, such as high surface tension, elevated viscosity, and maximum density at a specific temperature, render this ubiquitous liquid a molecular mystery, driving sustained studies across scientific disciplines [2,3]. Despite the ability to characterize these macroscopic properties through the persistent advancements in scientific instruments and theoretical methods, resolving the atomistic picture—particularly the structure of water—remains a significant challenges and continues to spark considerable debate.

The most fundamental question in gaining a microscopic comprehension of water is what are the structure and dynamics of the hydrogen bonding network. Experimental studies have primarily relied on characterization techniques including Raman spectroscopies [4,5], X-ray diffraction [6,7], and nuclear magnetic resonance [8], but remain constrained by limitations in temporal and spatial resolution [5]. Hence, a close synergy between theoretical methods and experimental results is imperative for a concerted effort toward a unified picture of water.

Computational science persists in developing a sufficiently accurate aqueous model, primarily carrying out molecular dynamics (MD) simulations with ab initio calculations or empirical force-field. [3, 9–20] It is thus not unexpected that numerous theoretical models of water have been reported in the literature, such as the TIPnP family [21–23], SPC [24, 25], q-AQUA [12–14] and MB-Pol [26]. Nevertheless, the density functional theory (DFT) holds its status as a cornerstone reference due to its exactness for ground-state properties in principle. A key point is that DFT in practice requires approximations to be made in the exchange-correlation energy, which critically governed the precision of calculations. The accuracy progressively improves along the Jacob's ladder of electronic structure theory, ascending from the local density approximation (LDA) through generalized gradient approximations (GGAs), meta-GGAs, and hybrid functionals, extending beyond to double hybrids, random phase approximation (RPA), and correlated wave function methods, such as second-order Møller-Plesset perturbation theory (MP2).

The selection for exchange-correlation functional exhibits considerable sensitivity in describing aqueous structural properties, from gas phase to solid. LDA is deemed unacceptable due to its overbinding of the water dimer, leading to an overstructured liquid water and a very small diffusion constant [27, 28]. GGA performs better than LDA, but still shows systematic errors in characterizing intermolecular water interactions. MD simulations at the GGA level, without dispersion corrections, require a substantial increase in temperature above 300 K to keep water in the liquid state. For example, PBE, a widely adopted functional, can reproduce experimental radial distribution functions (RDFs) and density at T = 440 K and P = 0.3 GPa, [29]. Even with the addition of Grimme's dispersion correction (DFT-D3) to PBE, which fails to markedly improve the structure of water [30], elevated temperatures are still required to reproduce these properties [30, 31]. BLYP-D3, with its reasonable performance in describing water properties [27], also requires simulations at 360 K to reproduce the correct RDF [32]. As a modification of the PBE functional, revPBE-D3 tends to perform best for RDF, density, and diffusion coefficient at ambient conditions without increasing the temperature [27, 30]. However, the results are highly sensitive to the particular choice of dispersion functional, as evidenced by the revPBE+DRSLL functional tending to overestimate the volume of ice VIII by 20%. [27] Recent developments in computational power and methodology have made it possible to climb higher rungs of the ladder beyond GGA, namely meta-GGA, hybrid functionals, and many-body correlated methods [33]. Perdew and co-workers proposed the non-empirical SCAN meta-GGA functional achieves remarkable accuracy for weak interaction systems [34]. SCAN functional yields the correct ordering of densities between liquid water and ice, at the same time predicting quantitative agreement with experiments at an elevated temperature of 330 K [35]. Despite its relatively higher accuracy, the bare SCAN functional still systematically overbinds water clusters [36]. Moreover, adding rVV10 to SCAN further exacerbates the overbinding, leading to a noticeable over- estimation of the density of liquid water [37]. Building on methods refinements, density-corrected SCAN calculation, presented by Paesani and co-workers, has improved accuracy to a level comparable to the "gold standard" coupled-cluster theory, which correctly describes water from the gas to the liquid phase through minimizing density-driven errors [36]. Simultaneously, some empirically parametrized meta-GGA functionals such as B97M with rVV10 correction also appear to perform quite well [38].

At hybrid functional level, the revPBE0-D3 functional is able to predict the correct experimental RDF and density at room temperature [39]. However, revPBE0-D3 still un- derestimates the temperature-dependent density of water by about 5% [40], which may be attributed to the choice of van der Waals interactions. The hybrid functional combined with rVV10 van der Waals interactions better reproduced the experimental equilibrium density of water through fine-tuning the empirical parameter [41]. Beyond hybrid functionals, including virtual orbitals allows for long-range van der Waals dispersion interactions from parameter-free ab-initio calculations. With tremendous computational cost, one can reach the fifth rung of the ladder with methods such as RPA and MP2. The MP2 theory, incorporating stronger dispersion interactions, provides excellent predictions of the density at room temperature and calculates radial distribution functions that are in reasonable agreement with experimental data [42]. Previous studies suggest that "MP2 water" is denser and cooler at ambient conditions compared both with experiment and with "DFT water" [43]. In addition to the underlying electronic structure theory, another issue is the accurate account of the quantum nature of the nuclei [44,45]. Due to the light mass of hydrogen nuclei, neglecting the pronounced nuclear quantum effects (NQEs) in aqueous systems [45]. The competition between intermolecular and intramolecular quantum effects, along with the challenge of accurately assessing these NQEs, could be one of the largest sources of errors [46,47]. For instance, the inclusion of NQEs induces subtle differences in RDFs, especially those that involve hydrogen atoms [44]. In a classical simulation, to produce a change in the RDF equivalent to that obtained by considering NQEs, the temperature has to be increased approximately 30 K [10,35]. Proton fluctuations along the covalent bond direction in quantum simulations also increase almost 10-fold. In addition, Voth et al. verified that higher temperatures do not accurately replicate NQEs at room temperature, which is evident in different three-body correlations as well as dynamics. [48] Regarding the reactivity of water, "classical" water is more basic than "quantum" water (i.e., water in nature) with a pH of 8.6, which is about a 30-fold change in the ionization constant [44]. Similar phenomena have also been