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# The influence of temperature and density functional models in *ab initio* molecular dynamics simulation of liquid water

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The performance of density functional theory methods for the modeling of condensed aqueous systems is hard to predict and validation by *ab initio* molecular simulation of liquid water is absolutely necessary. In order to assess the reliability of these tests, the effect of temperature on the structure and dynamics of liquid water has been characterized with 16 simulations of 20 ps in the temperature range of 280–380 K. We find a pronounced influence of temperature on the pair correlation functions and on the diffusion constant including nonergodic behavior on the time scale of the simulation in the lower temperature range (which includes ambient temperature). These observations were taken into account in a consistent comparison of a series of density functionals (BLYP, PBE, TPSS, OLYP, HCTH120, HCTH407). All simulations were carried out using an *ab initio* molecular dynamics approach in which wave functions are represented using Gaussians and the density is expanded in an auxiliary basis of plane waves. Whereas the first three functionals show similar behavior, it is found that the latter three functionals yield more diffusive dynamics and less structure. © 2005 American Institute of Physics. [DOI: 10.1063/1.1828433]

## I. INTRODUCTION

Liquid water is perhaps the most popular system in computational chemistry in terms of the effort spent on modeling its properties. Numerous force fields have been designed ranging from empirical models with parameters fitted to experimental data to *ab initio* models which have been parametrized using the results of quantum chemistry calculations of clusters in vacuum. The modeling of water has assumed a similar stimulating role in the development of *ab initio* molecular dynamics methods for aqueous systems. Since the first Car-Parrinello simulations of bulk liquid water about 10 years ago,<sup>1</sup> a succession of studies has appeared<sup>2–9</sup> using a variety of density functionals and molecular dynamics schemes. Repeating the history of classical simulation, the results of these *ab initio* simulations can show significant disagreement with experiment and among each other. Obviously, differences between current density functionals are an important source of discrepancy. However, the reproducibility and accuracy of the *ab initio* molecular dynamics methodology have also been questioned.<sup>6,8</sup> This was prompted by the observation that, even if the same density functional is used, a noticeable degree of variability in the structural (the pair correlation function) and dynamical (the diffusion con-

stant) properties remains. This suggests that these discrepancies should be contributed to more technical factors such as system size, duration of the run, and differences in implementation of the molecular dynamics (MD) method, including size and type of the basis set, pseudopotential, convergence criterium for the electronic structure calculation (Born-Oppenheimer MD) or fictitious mass (Car-Parrinello MD), time step, integrator, and ensemble. Indeed, in Ref. 8 it was shown that a proper choice of fictitious mass is vital for simulations of liquid water.

As *ab initio* simulations move towards more complex systems, this source of error needs to be understood. With a 300-fold increase of supercomputer power since the original publications,<sup>10</sup> a new generation of more systematic studies has become feasible, and we should be in a better position to resolve these issues. Thus, in a recent comprehensive study we have addressed the question of the convergence of the adiabatic force calculation. Results produced by the Car-Parrinello method were compared to results obtained by the Born-Oppenheimer MD method and Monte Carlo.<sup>9</sup> In the latter two approaches the electronic structure is recomputed every time step by iterative electronic minimization, in contrast to the Car-Parrinello method which applies a dynamical optimization scheme based on an extended Lagrangian ap-

proach. It was found that for the BLYP density functional<sup>11,12</sup> these three rather different methods could be made to agree provided the parameters controlling the accuracy were appropriately chosen.

The aim of the present study is to investigate to what extent the intricacies of the liquid itself could have aggravated the observed variability. This was motivated by the observation that temperature strongly affects the reproducibility of the results. System size was found to be a comparatively less sensitive variable. To investigate the influence of temperature in a more systematic fashion we have performed a total of over 600 ps of *ab initio* Born-Oppenheimer molecular dynamics simulations spread over a temperature interval of 280–380 K. The density functional we used was again BLYP. Anticipating our results we found that 325 K is a critical temperature for the time domain accessible in these runs (20 ps). The scattering in the results for temperatures below this value is significantly larger indicating that the relaxation times in (BLYP) water have become too long. The various computations of structural and dynamical properties supporting this claim are the subject of the first half of the paper, which also presents a systematic study of the influence of the basis set on structural and dynamical properties in the condensed phase, and illustrates the stability of the new Gaussian based *ab initio* molecular dynamics method employed in these simulations. The identification of an effective lower limit of the stability of liquid water has also enabled us to avoid some of the previous inconsistencies in evaluation of density functionals. Returning to the question of the quality of density functionals, we have compared six recent or commonly used density functionals, including one meta-GGA (GGA–generalized gradient approximation).<sup>13</sup> The results of this investigation are reported at the end of this paper.

## II. VALIDATION OF METHODS AND GAUSSIAN BASIS SETS IN THE CONDENSED PHASE

### A. Electronic structure computation and molecular dynamics

The simulations in this paper have been performed using a recently developed hybrid Gaussian plane wave (GPW) scheme that combines a Gaussian basis for the wave functions with an auxiliary plane wave basis set for the density as implemented in the CP2K/QUICKSTEP program.<sup>14–16</sup> The method is reviewed in detail in Ref. 16 and our computational setup mirrors closely the one described there. The advantage of the GPW method is that the Kohn-Sham matrix can be constructed in near linear scaling time maintaining the accuracy of conventional schemes. Similar to plane wave methods, the GPW approach makes use of pseudopotentials to represent core electrons. The pseudopotentials are of the Goedecker-Teter-Hutter (GTH) type, as determined initially for the local density approximation<sup>17,18</sup> and adjusted for the various density functionals employed in this study. Elements of the Kohn-Sham and overlap matrix smaller than  $\epsilon_{\text{default}} \approx 10^{-12} - 10^{-14}$  are neglected, and a 280 Ry density grid has been employed.

The majority of Density Functional Theory (DFT) based

plane wave molecular dynamics studies of water have employed the Car-Parrinello method. Born-Oppenheimer (BO) MD has been relatively rare (see, for example, Refs. 4 and 6). The current study also uses BO MD. A special technical feature of the current implementation in the CP2K code is the wave function extrapolation and optimization method developed by the authors of Ref. 19 (see also Ref. 16). This technique greatly enhances the efficiency of the BO molecular dynamics. The nuclear equations of motion have been integrated using a standard velocity Verlet algorithm with a 0.5 fs time step and hydrogen masses.

The model system consisted of 32 molecules in a cubic simulation cell with edges of 9.8528 Å under periodic boundary conditions. After equilibrating using classical force field methods, the initial configuration was equilibrated for at least 15 ps more using the BLYP (Refs. 11 and 12) density functional, prior to use in the production runs. The final runs, of which the first few picoseconds have been discarded for computation of properties, are all continuous NVE trajectories, i.e., without intermediate rescaling of the ionic velocities. We enforce a sufficiently strict convergence upon the wave functions (convergence criterium for the electronic gradient  $\epsilon_{\text{SCF}} \approx 10^{-6} - 10^{-7}$ , energy difference between final self-consistent field (SCF) cycles  $10^{-10} - 10^{-12}$  a.u. per atom), so that the drift in the total energy during these simulations is  $\approx 10^{-6}$  a.u./ps/atom. For the water systems considered, this is equivalent to a temperature change of  $\approx 1$  K over a 10 ps simulation and suggests that the correct NVE ensemble is sampled.

The mean square displacement (MSD) curves were computed from the relative displacements of the oxygen atoms only, averaged over all water molecules and all configurations of the full trajectory as starting points. Frames of the trajectory have been stored every 2 fs. The slope of the curves has been estimated by a linear fit to the data, starting from about 2 ps to about half the length of the trajectory. This avoids the final part, where the average is only over few uncorrelated frames, and the initial rapidly increasing part that is due to the motion of the molecules in their solvation cages. Nevertheless, the statistical uncertainty might still be relatively large, in particular, if the system is not diffusive. The pair correlation functions  $[g(r)]$  have been computed using a binning width of 0.03 Å, as suggested in Ref. 5, and are not smoothed.

### B. Basis set convergence

In the GPW method, as in other localized basis set calculations, the quality of the Gaussian basis set is an important issue. In fact, there is little information about the performance of a Gaussian basis set in the context of molecular dynamics simulations of liquids. It is well known that the basis set superposition error (BSSE) can be a significant fraction of the binding energy of the water dimer, which could affect liquid simulations.<sup>20</sup> However, the effect of BSSE on structural and dynamical properties of the liquid has not been investigated previously. In order to quantify the influence of the basis set on the pair correlation functions and the diffusivity of the liquid, we have explicitly performed simulations

TABLE I. Characteristics of an OLYP simulation [Gaussian basis functions per molecule (BF), time length, temperature, energy drift in a.u. $\times 10^{-6}$ /(ps/atom)] and computed properties [slope of the mean square displacement curves (MSD)], maximum of the oxygen-oxygen pair correlation function for six different basis sets with the same strict convergence criterion ( $\epsilon_{\text{SCF}}=10^{-7}$ ) and two simulations with a less strict convergence criterion ( $\epsilon_{\text{SCF}}=10^{-6}$ , last two lines with the LC postfix.).

Basis	BF	Time (ps)	$T$ (K)	Drift	MSD ( $\text{\AA}^2 \text{ps}^{-1}$ )	$g(r)_{\text{OO}}^{\text{max}}$
DZVP	23	22.2	300	0.2	1.35	2.16
TZVP	29	18.7	311	0.6	0.78	2.33
TZV2P	40	21.2	311	0.8	0.77	2.27
QZV2P	46	16.1	306	0.5	0.78	2.19
OPT-TZVP	29	12.8	315	0.3	0.67	2.28
OPT-TZV2P	40	12.5	305	0.6	0.88	2.07
TZV2P-LC	40	24.6	308	-1.5	0.63	2.25
OPT-TZV2P-LC	40	21.4	306	-2.4	1.07	2.16

of 32 water molecules using six different basis sets (DZVP, TZVP, TZV2P, QZV2P, OPT-TZVP, OPT-TZV2P) with the OLYP (Ref. 21) functional.

The results are summarized in Table I. The DZVP, TZVP, TZV2P, and QZV2P basis sets have been constructed with a split valence method,<sup>16</sup> whereas in the OPT-TZVP and OPT-TZV2P basis sets the contractions of both valence and polarization functions (over six Gaussian exponents) have been optimized explicitly to yield the lowest total energy for a liquid configuration, while retaining a low condition number of the overlap matrix. These optimized basis sets are computationally more demanding and the corresponding trajectories are somewhat shorter (see Table I). We have also computed two trajectories with a lower convergence (LC) of the wave function at every BO step.

The data reported in Table I show that MSDs and the maximum of the pair correlation function are in good agreement with each other for all the methods. The small deviations are well within the statistical uncertainty (see below), except perhaps for the DZVP basis which appears to yield a slightly more diffusive liquid. The insensitivity of the results is rather remarkable and deserves further study. In the remainder of this study we have employed TZV2P and QZV2P basis sets, with 1280 and 1472 basis functions for 32 water molecules, respectively, for  $\approx 10^7$  SCF cycles.

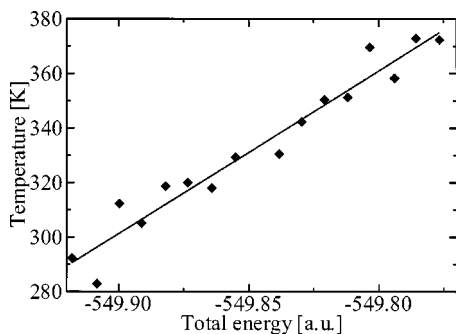


FIG. 1. Relationship between total energy and average temperature for the 16 NVE simulations of 32 water molecules as described in detail in the text. The solid line is a linear fit through the data.

### III. TEMPERATURE DEPENDENCE OF PROPERTIES OF BLYP WATER

In order to investigate the effect of temperature on BLYP water we have set up 16 systems with different total energy, keeping all other parameters fixed. The total energy was chosen to yield final average temperatures in the range 280–380 K. The first eight trajectories were started from the same 300 K equilibrium configuration (with different velocities), whereas the later eight trajectories were initiated from one of the resulting configurations that equilibrated near 330 K. All 16 simulations are  $\approx 20$  ps long. A TZV2P basis has been employed, and  $\epsilon_{\text{SCF}}=10^{-6}$  resulting in an energy drift in the order of  $10^{-6}$  a.u./ps/atom. As shown in Fig. 1 the relationship between the total energy and the temperature of these runs is effectively linear. The maximum fluctuations around the expected value (fitted line) are on the order of 10 K which can be considered as the statistical uncertainty in the temperature for runs of 32 water molecules and 20 ps duration.

The resulting oxygen–oxygen pair correlation functions are shown in Fig. 2. The change in shape of the curves clearly reflects the strong effect of temperature on the structure of water. The temperature dependence of the features of

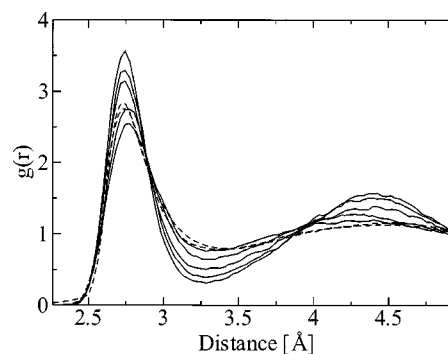


FIG. 2. Shown are 5 out of 16 oxygen–oxygen pair correlation functions, corresponding to simulations with temperatures of 292, 318, 329, 351, and 372 K. The ordering of the curves follows the expected behavior, i.e., minima and maxima become less pronounced and positions of the first peak shift outwards for increasing temperatures. This is further quantified in Fig. 3. The dashed lines are the experimental results from Refs. 28 and Ref. 29.

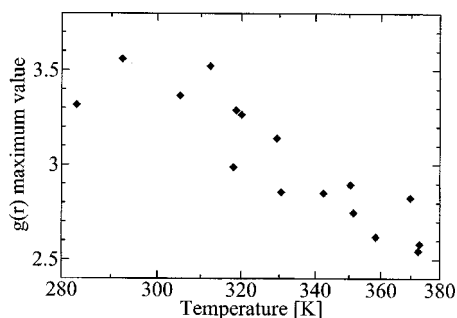


FIG. 3. Temperature dependence of the maximum value for the first peak of the 16 oxygen–oxygen pair correlation functions five of which are shown in Fig. 2.

the curve, such as heights and positions of minima and maxima, is in agreement with the expected smoothing of the curves with increasing temperature. In Fig. 3 this is quantified for the maximum of the first oxygen–oxygen peak. A wide range for the maximum can be observed (2.5–3.6), and we note that the scatter in the results is not small.

The MSDs obtained from these simulations, shown in Fig. 4, exhibit an even more pronounced sensitivity to temperature. The MSDs lie in the range  $1.0\text{--}0.001 \text{ \AA}^2 \text{ ps}^{-1}$ , with a roughly exponential dependency on the inverse temperature. Furthermore, it is apparent from the outliers that these BLYP simulations suffer from nonergodic behavior on the 20 ps time scale of the simulation at temperatures below  $\approx 325 \text{ K}$ . We note that this temperature might depend on simulation parameters such as system size and density functional. In this regime, configurations can remain in nondiffusive or more liquidlike state for long times. These low temperature results can therefore not be converged within the 20 ps time scale and are very sensitive to the initial conditions, even if the simulation setup is identical. This makes simulations at these conditions very sensitive to all simulation details, including, e.g., the equilibration or thermostating method. This behavior, combined with the difficulty of estimating the temperature of short runs, can be part of the explanation for the inaccuracies in results reported in literature. We note also that experimentally the diffusion and observed peak heights are strongly dependent on the temperature, es-

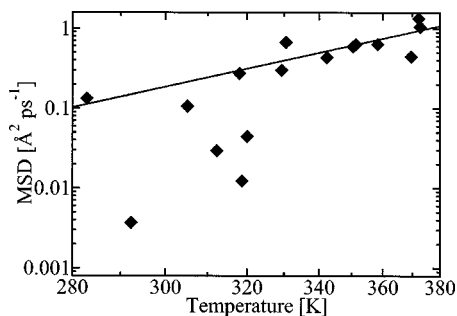


FIG. 4. Slopes from the MSD curves obtained for the 16 water simulations described in the text. The gray line is an Arrhenius fit to data points  $> 325 \text{ K}$ . The activation energy obtained in this way is  $21 \text{ kJ/mol}$  with an uncertainty of about  $5 \text{ kJ/mol}$ . Significant deviations from the extrapolation can be observed in the lower temperature range. These deviations are indicative of nonergodicity at lower temperatures.

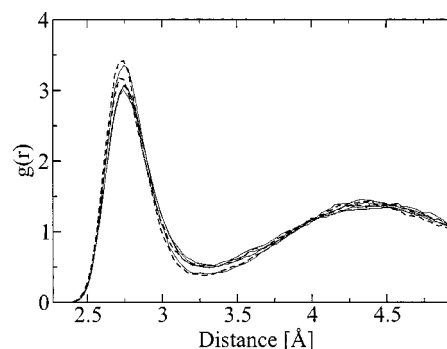


FIG. 5. The oxygen–oxygen pair correlation functions for four simulations of 64 water molecules (solid lines) are compared with the results for 32 water molecules (dashed lines). The two more structured curves are for simulations with a temperature near  $305 \text{ K}$ , whereas the four less structured curves are for temperatures near  $330 \text{ K}$ . The three solid lines that are nearly indistinguishable are simulations with slight changes in the unit cell ( $12.40$ ,  $12.42$ ,  $12.44 \text{ \AA}$ ) and this indicates that such changes have little effect on the structure of liquid water. The relatively good agreement between the simulations at the same temperature but different particle number indicates that size effects are small and that the temperature dependence observed for 32 water molecules carries over to 64 water molecules.

pecially if the metastable supercooled water is considered as well.<sup>22,23</sup> Note that our simulations have been performed at constant volume, whereas these experiments are at constant pressure.

System dimensions are another set of critical parameters in simulation. In order to probe the response to an increase in system size, we have performed four simulations of a 64 molecule system using a computational setup as for the other simulations in this section. These trajectories are only 10–13 ps long. Three have average temperatures of  $335$ ,  $329$ , and  $328 \text{ K}$ , whereas one has a temperature of  $306 \text{ K}$ . Moreover, the density used in the literature is subject to small variation. In order to span this uncertainty the three runs at higher temperatures were carried out in cells of slightly different size (the edges of the cubic cell are  $12.40$ ,  $12.42$ , and  $12.44 \text{ \AA}$ ). The cell size of the lower temperature run is  $12.42 \text{ \AA}$ . The results of these simulations are shown in Figs. 5 and 6 for pair correlation functions and MSD, respectively. Based on this (limited) evidence, it seems that system size effects

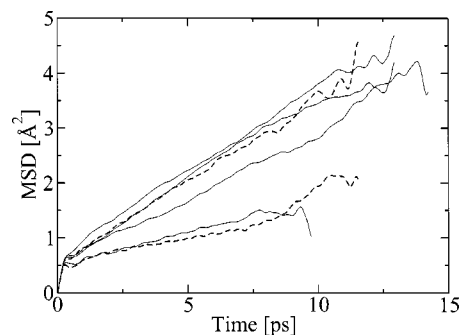


FIG. 6. Mean square displacements for the systems described in Fig. 5. The solid lines correspond to simulations with 64 water molecules, the dashed lines to simulations with 32 water molecules. The lower two lines correspond to temperatures near  $305 \text{ K}$ , whereas the four upper curves are for simulations near  $330 \text{ K}$ . There is no trend corresponding to the variations in unit cell.

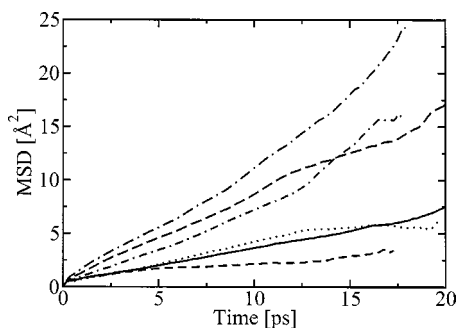


FIG. 7. MSDs as obtained for simulations with the BLYP, PBE, TPSS, OLYP, HCTH120, and HCTH407 functionals using solid, dotted, dashed, long dashed, dash dotted, and long dash dotted lines, respectively.

and the influence of small unit cell changes are not very pronounced for the properties considered. At the same time, the observed temperature dependence appears to be transferable to these larger systems.

#### IV. PERFORMANCE OF SIX DIFFERENT DENSITY FUNCTIONALS

After this preparation, let us now return to the question of the accuracy of density functionals for liquid water. This has been tested previously (see, e.g., Refs. 2 and 24), but the significant increase of computing power and the efficiency of our scheme allows for longer production runs and longer equilibration. Simulations have all been started from the same initial configuration, with the same initial velocities, same basis (QZV2P), and convergence settings ( $\epsilon_{\text{SCF}} = 10^{-7}$ ), but with different density functionals. The initial configuration and velocities were taken from a BLYP run at  $\approx 330$  K, so that the nonergodic region, at least for the BLYP functional, is avoided. The length of all runs is again  $\approx 20$  ps. The functionals we have investigated are BLYP,<sup>11,12</sup> PBE,<sup>25</sup> TPSS,<sup>13</sup> OLYP,<sup>21</sup> HCTH120,<sup>24,26</sup> HCTH407.<sup>26,27</sup> The TPSS functional is a recent meta-GGA and explicitly introduces the kinetic energy density  $\tau$  in the exchange and correlation energy. A PBE pseudopotential has been employed for the TPSS simulations. Comparing bond lengths for a set of dimers to all electron calculations and repeating the simulations of the liquid with a BLYP pseudopotential (data not shown), we verified that the influence of the pseudopotential is negligible.

The results are shown in Figs. 7 and 8 and summarized in Table II. The strong variations between the different func-

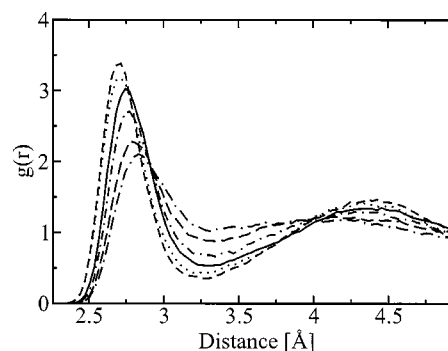


FIG. 8. Oxygen–oxygen pair correlation functions as obtained for simulations with the BLYP, PBE, TPSS, OLYP, HCTH120, and HCTH407 functionals indicated by solid, dotted, dashed, long dashed, dash dotted, and long dash dotted lines, respectively.

tionals are unambiguous. The MSD derived from the BLYP, PBE, and TPSS simulations clearly point to a too sluggish dynamics, which is consistent with overstructuring of the pair correlation functions. The three other functionals are significantly more diffusive and correspondingly less structured. However, OLYP and HCTH407 exhibit too little structure to compare well with experiment. These results are even more striking if one considers the temperatures (Table II) to which these runs equilibrate. Indeed, e.g., the diffusion of HCTH407 is about twice as fast as the diffusion of PBE, even though the later run is at about a 30 K higher temperature. The fact that, starting from the same configuration and velocities, some simulations equilibrate to a lower temperature is consistent with their more “liquid like” behavior.

#### V. CONCLUSION

We have investigated the effect of temperature and different choices of density functional on results obtained from *ab initio* simulations of liquid water under carefully controlled conditions. These simulations show that current functionals may yield qualitatively different predictions for properties of the neat liquid. In the light of the results available in literature about DFT performance in the gas phase, this is not a surprise. However, as extrapolation from dimer calculations to the liquid proves unreliable, the implication is that testing and deciding upon an appropriate functional is necessary when simulating aqueous systems. In spite of these shortcomings, and if the somewhat empirical approach to circumvent them is accepted, DFT provides a reasonable de-

TABLE II. Characteristics [time length, temperature, energy drift in  $\text{a.u.} \times 10^{-6}/(\text{ps}/\text{atom})$ ] and computed properties [mean square displacement (MSD), maximum of the oxygen-oxygen pair correlation function] for a 32 molecule system comparing six different density functionals. Experimentally, at room temperature, the MSD is  $1.3 \text{ \AA}^2/\text{ps}$  and  $g(r)_{\text{OO}}^{\text{max}}$  is 2.8.

DFT	Time (ps)	$T$ (K)	Drift	MSD ( $\text{\AA}^2 \text{ps}^{-1}$ )	$g(r)_{\text{OO}}^{\text{max}}$
BLYP	22.0	324	0.7	0.31	3.03
PBE	20.3	337	1.4	0.40	3.18
TPSS	18.1	351	3.4	0.14	3.38
OLYP	21.2	310	1.0	0.75	2.29
HCTH120	18.6	315	1.2	0.65	2.71
HCTH407	18.8	307	1.0	0.94	2.11

scription of the liquid and is able to deal with the tiny energy scales involved. Our relatively long simulations confirm the results of previous work<sup>6,8,9</sup> that the application of either BLYP or PBE functionals leads to more structure and a more sluggish dynamics than that anticipated in earlier simulations, based on shorter trajectories. The same holds for TPSS, a recent meta-GGA. From a practical point of view, a more diffusive liquid, such as obtained with OLYP, HCTH120, and HCTH407 is a significant advantage for modeling reactions in solution, as the time scales needed to sample solvent configurations become shorter and equilibration becomes faster.

In agreement with experimental work, we have observed strong temperature dependence of structural and dynamical properties. This should be kept in mind while performing simulations of water at ambient conditions, i.e., close to the triple point. Part of the discrepancies in the literature can be explained by the uncertainty in the temperature estimate of relatively short simulations and the risk of poor equilibration violating equipartition. Furthermore, even for the runs of the order of 20 ps as performed in this study, the observed non-ergodic behavior for the BLYP simulations at lower temperature should be taken into account when deciding on the simulation protocol. While our results confirm that the *ab initio* molecular dynamics technique is not yet a black box tool for the condensed phase, we remain convinced of the merits and strengths of the method.

## ACKNOWLEDGMENTS

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