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M. A. Morales, J. R. Gergely, J. McMinis, J. M. McMahon, J. Kim, D. M. Ceperley

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Quantum Monte Carlo benchmark of exchange-correlation functionals for bulk water

Miguel A. Morales,[1,*] John R. Gergely,[2] Jeremy McMinis,[1]
Jeffrey M. McMahon,[2] Jeongnim Kim,[3,4] and David M. Ceperley[2]

[1]*Lawrence Livermore National Laboratory, Livermore, California 94550, USA*

[2]*Department of Physics, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA*

[3]*Material Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA*

[4]*Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA*

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Abstract

The accurate description of the thermodynamic and dynamical properties of liquid water from first-principles is a very important challenge to the theoretical community. This represents not only a critical test of the predictive capabilities of first-principles methods, but it will also shed light into the microscopic properties of such an important substance. Density Functional Theory, the main workhorse in the field of first-principles methods, has been so far unable to properly describe water and its unusual properties in the liquid state. With the recent introduction of exact exchange and an improved description of dispersion interaction, the possibility of an accurate description of the liquid is finally within reach. Unfortunately, there is still no way to systematically improve exchange-correlation functionals and the number of available functionals is very large. In this article we use highly accurate quantum Monte Carlo calculations to benchmark a selection of exchange-correlation functionals typically used in Density Functional Theory simulations of bulk water. This allows us to test the predictive capabilities of these functionals in water, giving us a way not only to choose optimal functionals for first-principles simulations, but also giving us a route for the optimization of the functionals for the system at hand. We compare and contrast the importance of different features of functionals, including the hybrid component, the vdW component, and their importance within different aspects of the PES. In addition, we test a recently introduce scheme that combines Density Functional Theory with Coupled Cluster Calculations through a Many-Body expansion of the energy, in order to correct the inaccuracies in the description of short range interactions in the liquid.

PACS numbers:

I. INTRODUCTION

Water is a unique substance. Not only is it ubiquitous to life and plays a critical component to almost all chemical, biological, and geophysical processes, it plays a principal role in many fields of physics including surface physics, energy production, geology, planetary science, high-pressure physics, and numerous others[1]. Even after intense efforts for many decades, from both theoretical and computational approaches, the prediction of water's properties at ambient conditions remains a challenge. Despite its apparent simplicity, liquid water possesses a set of anomalous and fascinating properties, mainly related to a non-monotonous dependence of thermodynamic and dynamical properties with temperature (e.g. a minimum in the isothermal compressibility)[2]. The description of these anomalous properties from first-principles remains a challenge to the theoretical community. The main problem lies in the non-trivial interaction between several subtle effects in the liquid, which include a strong directional hydrogen bonding between neighboring molecules, weaker but important dispersion interactions, and strong nuclear quantum effects (NQE). These unusual properties, together with the vast array of physical processes occurring in the liquid, make water a very complicated but essential substance to understand using an atomic scale description.

Within the Born-Oppenheimer approximation at low temperatures, the only interaction between ions and electrons comes through the potential energy surface $E_0(\mathbf{R})$, defined as the solution of the electronic hamiltonian for a fixed set of ionic coordinates. This approximation reduces the calculation to two independent parts, the accurate calculation of $E_0(\mathbf{R})$ (the electronic structure problem) and the integration over $\mathbf{R}$ (NQE). As shown recently, NQEs can be treated accurately and efficiently in combination with first-principles electronic structure methods in condensed systems using a path integral representation[3–5]. The PIMD+GLE method[6], which involves the use of colored thermostats combined with a PIMD representation leads to a particularly efficient simulation methodology. With the use of PIMD methods, the largest remaining source of approximations in first-principles simulations of liquid water comes from the calculation of $E_0(\mathbf{R})$. Due to its favorable ratio between accuracy and computational cost, DFT has become the workhorse in the field. The quality of $E_{DFT}(\mathbf{R})$ defines the predictive capabilities of the resulting first-principles simulation. In fact, the recent explosion in the popularity of first-principles methods is, to a large part, due

to the success of DFT in providing a fairly accurate description of the electronic structure, and a large range of observables, at a reasonable computational cost.

While DFT has been very successful in the description of many types of systems, e.g. metals and weakly correlated systems, many of the currently available exchange-correlation functionals in DFT possess well-known limitations[7], including the failure to properly describe strongly correlated materials, self-interaction errors, dispersion interactions, etc. It is recognized that even for water, the ab-initio molecular dynamics (AIMD) procedure is currently not accurate enough, giving large errors in many basic properties including the melting temperature, the diffusion constant, the compressibility, among others[8,9]. Nonetheless, much progress has occur during the last several years. The main advances include the use of functionals with an improved description of dispersion interactions in the liquid[10–14], the use of hybrid functionals[15], and the direct treatment of nuclear quantum effects[3]. The combination of all of these advances in first-principles simulations of liquid water could lead to an accurate description of its interesting properties and its local structure. At the same time, the choice of exchange-correlation functional in DFT is still a source of complication, mainly due to the large number of available choices and the inability to test their predictive capabilities without resorting to full first-principles calculations of a large set of observables.

With the fast increase in computational power and the development of improved algorithms, we are quickly approaching a time where we can go beyond mean-field methods in the simulation of bulk systems, using accurate many-body methods like many-body perturbation theory (MBPT), coupled-cluster (CC) and quantum Monte Carlo (QMC). Currently these methods remain too expensive for regular use in first-principles simulations of bulk systems, so we must resort to DFT. Nonetheless, both CC and QMC produce accurate results that can be used to both benchmark, and even improve DFT methods. While CC is more efficient for small clusters, QMC offers an advantage over CC in bulk calculations in terms of speed and scaling, in fact very few attempts have been made to apply CC to periodic systems. While local formulations of CC for finite systems exist with very favorable scaling, which offer considerable promise and could be extended to periodic systems in the near future, QMC is the only alternative for accurate many-body calculations of the energy of liquid water. QMC methods are generalizations of the classical Monte Carlo techniques to quantum statistical physics and are fundamentally based on imaginary-time path integrals. For a class of systems (bosons, one dimensional physics) such techniques provide an exact

computational method. For general problems, while not exact, they are highly accurate *and* systematically improvable. In the case of water and other weakly bounded systems, there is a growing literature that shows the high accuracy of the method[16–19].

Finite-temperature first principles simulation methods entirely based on QMC have also been developed in the last decade. These are the Coupled Electron-Ion Monte Carlo method[20,21] and the QMC-Molecular Dynamics[22], and have been recently reviewed in[23]. However their application to condensed phases has been limited so far to high pressure hydrogen, and hydrogen-helium mixtures because of the considerable computation cost of those methods. While it is highly desirable to have QMC-based FP simulations that could be applied routinely to arbitrary systems, this is probably not possible in the near future. We need a way to incorporate the accuracy of these methods in more efficient mean-field methods such as DFT. We propose one way to achieve this in this article: use QMC to benchmark DFT functionals. This not only allows us to measure the accuracy of DFT before its use in first-principles simulations, but also it paves the way for the development of functionals from reference QMC calculations. While this is done routinely for finite molecular systems, using CCSD(T) as a reference for example, we show how this could also be done in bulk systems with QMC.

In this work we present a comparison between QMC calculations and various DFT exchange-correlation functionals on water at ambient conditions. We also discuss the use a recently introduced correction scheme for DFT energies using a cluster decomposition of the energy of the system combined with CC calculations on small clusters[24,25]. As we show below, this offers a very promising and efficient alternative to hybrid functionals, potentially leading to functionals with unprecedented accuracy in the description of liquid water. The article is organized as follows: section II describes the details of the various computational methods used in the calculations present in this work, section III presents the main results of the comparison between QMC and DFT in bulk water configurations along with the corresponding discussion, this is followed by a conclusion in section IV.

II. COMPUTATIONAL DETAILS

In this article we present a benchmark of the accuracy of various DFT functionals typically used to simulate bulk water. To do this, we first generate various sets of water configurations

from both MD and PIMD simulations of bulk water in the liquid and ice phases near ambient density. For all of the configurations in the various test sets, we calculate QMC and DFT energies, with the various functionals. We compare QMC and DFT calculations on a diverse collection of test sets in order to sample the performance of DFT throughout the configuration space that ambient water might reasonably be expected to sample.

Eight different sets of configurations were studied, each one produced from a different type of simulation. Both classical and quantum simulations are used, as well as several types of ionic interactions. A summary of the details of the simulations used to generate configurations is presented in Table II. The Forced Matched potential used in the configuration set *FM.25C* was produced by Huang and Schwegler[26]. It uses the same rigid molecular geometry as SPC[27] with electrostatic charges of -0.48 on the oxygen site and 0.24 on the hydrogen sites. However, the core repulsion is not maintained with a Lennard - Jones interaction. Instead, there is a pairwise spline potential between each pair of interacting sites (OO, OH, HH). The OO spline potential contains a strong repulsion at small r and a shallow attractive region, similar to a Lennard - Jones interaction. The OH and HH splines are relatively weak compared with other interactions in the system, but they are meant to capture hydrogen bonding characteristics of the many - body system. The forced matched potential is parametrized by matching the model forces with those from DFT-GGA calculations. Therefore, it is designed to be an *ab initio* - like potential that closely resembles results from *ab initio* electronic structure calculations. TIP5P refers to the empirical water model of Mahoney *et al.*[28], while vdW-DF refers to DFT calculations with the non-local exchange-correlation functional of Dion, *et al.*[10,29,30] and vdW-DF2 refers to its revised version by Lee *et al.*[11]. While TIP5P and the Force Matched potential are rigid molecule models, the first-principles simulations with vdW-DF and vdW-DF2 are fully flexible, which allows us to differentiate different ranges of the molecular interactions in the liquid. On the other hand, the simulations with the TIP5P model on liquid and ice at $T = 0°$C sample configurations that either strongly favor hydrogen bonding in the solid, with those where the hydrogen-bond network has been destabilized in the liquid.

DFT calculations were performed with both Quantum Espresso (QE)[31] and VASP[32] simulation packages. In the case of QE calculations we employed Ultra-Soft pseudo-potentials (USPP)[33,34], while in the case of VASP calculations we employed the Projector Augmented Wave method (PAW)[35,36]. In both cases, we used USPP and PAW from the standard distri-

Label	# mols	# confgs	T (°C)	Ion Interaction	Classical/Quantum	State	Flexible
FM.25C	32	30	25	Force Matched	Classical	Liquid	No
TIP5P.CL.25C	32	23	25	TIP5P	Classical	Liquid	No
TIP5P.PI.0C.ICE	32	20	0	TIP5P	Quantum	Solid	No
TIP5P.PI.0C.LIQ	32	47	0	TIP5P	Quantum	Liquid	No
TIP5P.PI.100C	32	44	100	TIP5P	Quantum	Liquid	No
TIP5P.PI.25C	32	18	25	TIP5P	Quantum	Liquid	No
PIMD-vdW-DF	64	50	27	vdW-DF	Quantum	Liquid	Yes
PIMD-vdW-DF2	64	50	27	vdW-DF2	Quantum	Liquid	Yes

TABLE I: Summary of the details of the simulations used to generate the configurations in this study. The labels defined in the first column will be used throughout the paper to refer to the given configuration set.

Label	$L(\mathring{a})$
FM.25C	9.8625
TIP5P.CL.25C	9.8625
TIP5P.PI.0C.ICE	9.697
TIP5P.PI.0C.LIQ	9.697
TIP5P.PI.100C	9.697
TIP5P.PI.25C	9.697

TABLE II: Simulation box lengths for NVT simulations of FM and TIP5P.

butions of the software packages generated with PBE. We verified that the final conclusions do not depend on this choice. A single pseudo-potential was chosen in order to make a homogeneous comparison of all DFT functionals, since some of the functionals employed in this work do not yet allow for the production of pseudo-potentials. All simulations were performed at the Γ point of the supercell in order to be consistent with the corresponding DMC calculations, errors due to the lack of k-point integration were on the order of 0.03 mHa/molecule (for the smaller unit cells), small enough to be safely discarded. The plane wave cutoffs were chosen to converge the total energies to better than 0.05 mHa/molecule.

In this article we consider some of the density functionals commonly used to simulate bulk water from first-principles. The list includes: *GGA's*: PBE[37], BLYP[45,46], OLYP[47]; *hybrid functionals*: PBE0[38], B3LYP[39,40]; *empirical dispersion corrected functionals*: PBE-D[41], BLYP-D[41], vdW-TS[42]; *non-local correlation functionals*: optB86b[43], optB88[44], optPBE[44], vdW-DF[10], vdW-DF2[11], VV10[48]; and *hybrid functionals with empirical corrections*: B3LYP-D. X-D, where X represents a given density functional, designates results using the empirical dispersion corrections of Grimme *et al.*,[41], in particular the DFT-D2 correction scheme as implemented in VASP and QE. The list of functionals covers the two most important features of advanced density functionals, hybrid functionals and improved dispersion interactions.

QMC has been shown to be a reliable benchmark in the study of small water clusters, producing relative energies with an accuracy comparable to that of CCSD(T)[16,24,49]. It provides an accurate reference method to measure the quality of typical density functionals used in simulations of bulk water. All DMC calculations were performed with the QMCPACK software package[50]. A Troullier-Martins norm-conserving pseudo-potential (TMPP)[51] was used to represent both hydrogen and oxygen. In particular, we used TMPPs from the CASINO pseudo-potential database[52,53], which were recently shown to produce accurate results in the study of small water clusters. A Slater-Jastrow trial wave-function was used. The orbitals in the Slater determinant were obtained from DFT calculations employing the PBE exchange-correlation functional. We compared DMC energies generated with various DFT functionals on a small subset of the configurations, the variation in relative energies was quite small. The Jastrow term contains electron-Ion, electron-electron and electron-electron-Ion terms, the variational parameters were optimized at the VMC level using a variant the linear method of Toulouse, *et al.*[54]. A time-step of 0.01 Ha^{-1} was found to be sufficiently small to produce accurate total energies and approximately 4800 walkers were used in the DMC calculations. Casula's T-moves[55] were used to reduce errors associated with the locality approximation, while the Model Coulomb Potential (MPC) of Fraser, *et al.*,[56] and Chiesa's[57] correction scheme were used to estimate finite-size corrections to the potential and kinetic energies respectively. Specifically, we performed the DMC calculations using the Coulomb interaction between electrons, and used the MPC interaction to estimate the magnitude of finite size effects on the potential energy.

III. RESULTS AND DISCUSSION

We use the mean absolute difference (MAD) with respect to the DMC energies as the main measure of accuracy for the different density functionals considered in this article. Since we are interested only in the ability of the different functionals to accurately reproduce relative energy differences between configurations within a given set and not on absolute energies, we measure the energy differences with respect to the average energy difference in the set. This is equivalent to shifting the zero of energy of each set so that it coincides with the corresponding one from DMC. Specifically, we define the MAD as follows:

$$MAD = \frac{1}{N_c} \sum_{i=1}^{N_c} \left| \left(E_i^{DFT} - E_i^{DMC}\right) - \left\langle E_i^{DFT} - E_i^{DMC} \right\rangle \right|, \tag{1}$$

where N_c is the number of configurations in the set, $E_i^{DFT}(E_i^{DMC})$ are the DFT (DMC) energies (in units of mHa/molecule), and $< E_i^{DFT} - E_i^{DMC} >= \frac{1}{N_c}\sum_{i=1}^{N_c}(E_i^{DFT} - E_i^{DMC})$ is the average energy difference in the set.

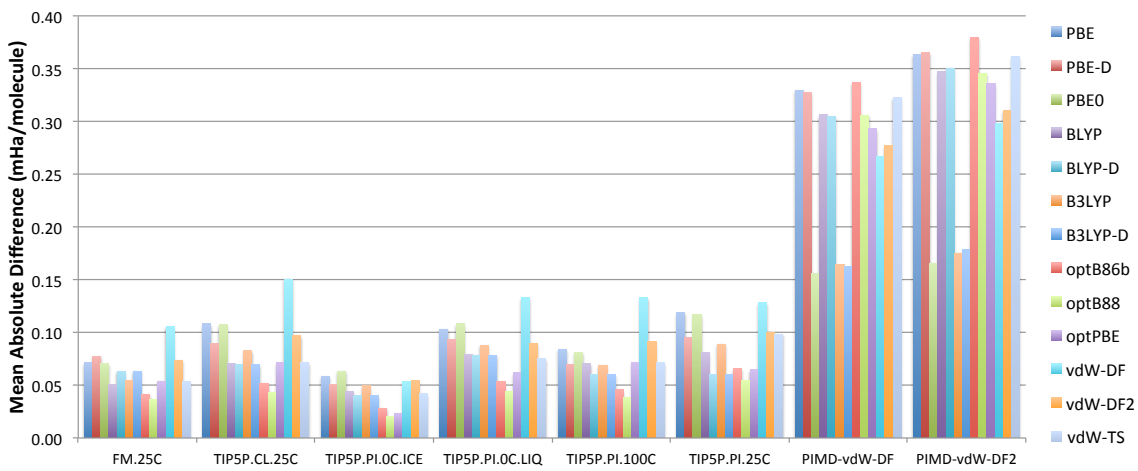

FIG. 1: (Color online) Mean absolute difference in the total energy between DMC and DFT with various exchange-correlation functionals. Results presented correspond to calculations using the PAW formulation with VASP. Error on the presented results are smaller than 0.004 mHa and 0.006 mHa for fixed and flexible molecule configurations respectively. They are not shown on the figure for clarity.

Figure 1 shows the MAD for all the density functionals studied with VASP in this work, results are separated by configuration sets to allow a better comparison. While there are

several significant results in the figure, the most noticeable feature is the large difference in the scale of the MAD between rigid and flexible molecule configuration sets. This is not completely unexpected since the larger energy fluctuations in the system are found coupled to the intramolecular degrees of freedom of the molecule (e.g. molecular vibrations). While this will, in general, complicate the analysis of the potential energy surface and the comparison between different methods, it nonetheless provides a positive point since it offers a very clear distinction for hybrid functionals.

In the case of flexible molecule configurations, hybrid functionals offer a much better agreement with DMC results, producing errors typically a factor of two smaller than non-hybrid functionals. These results shows the fact that hybrid functionals do a much better job at describing the intramolecular potential energy surface. This is consistent with the recent calculations of Gillan, *et al.*[16] and with the recent calculations of the absorption spectra of bulk water at ambient conditions of Zhang, *et al.*[15]. On the other hand, the functionals that include an appropriate description of dispersion interactions offer a better comparison with QMC in the rigid-molecule configuration sets. Intermolecular interactions are the dominant energy contribution on these sets and the lack of an appropriate description of dispersion interactions leads to a larger error. We can also see, on average, a small but finite improvement with the inclusion of empirically corrected vdW functionals (PBE-D, B3LYP-D), but the gain is small and cannot compete with non-local vdW functionals. Notice also that the performance of hybrids in the fixed-molecule sets is comparable to the performance of semi-local functionals, due to the fact that neither of these type of functionals can properly describe dispersion interactions. Finally, the configuration set with the smallest overall MAD is the one obtained from the calculations in the solid phase close to melting, illustrating that most of these functionals can describe hydrogen bonded configurations (dominant on this set) quite well.

When compared only across flexible or frozen water models, the average value of the MAD and its magnitude relative to other density functionals is, to a large degree, only slightly dependent on configuration set. Figure 2 shows the MAD for VASP calculations, now averaged over frozen and flexible configuration sets, which we denote by *TIP5P-32* and *PIMD-64*. For frozen molecule configurations, the optimized non-local vdW functionals perform the best, with the optB88 functional producing the best overall results. On the other hand, the vdW-DF functional has the worse performance; vdW-DF2 has a performance

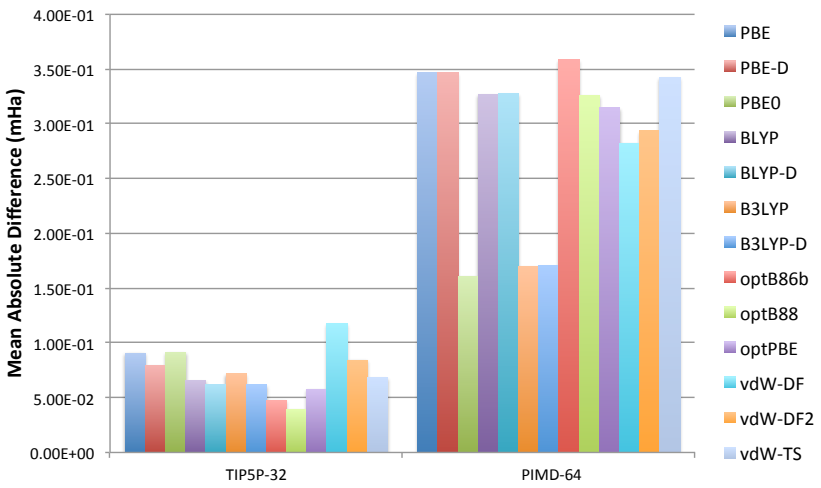

FIG. 2: (Color online) Mean absolute difference in the total energy between DMC and DFT with various exchange-correlation functionals. *TIP5P-32* refers to the average over all fixed molecule configuration sets, while *PIMD-64* refers to the average over all flexible molecule sets. Results presented correspond to calculations using the PAW formulation with VASP.

comparable to most of the GGAs studied. In the case of the flexible molecule sets, the picture is reversed. In this case, the vdW-DF functional offers the best performance of the non-hybrid functionals, followed by vdW-DF2. The optimized vdW functionals have a performance comparable to that of the GGAs.

As mentioned above, the comparison between the different density functionals is complicated by the non-trivial combination of multiple types of interactions in the liquid. While the use of frozen and flexible configuration sets present a clear distinction between the functionals from the point of view of dispersion interactions (dominant in the former) and the intramolecular interactions (dominant in the latter), it does not provide a definite picture of the relative accuracy of the different functionals. This is best exemplified when comparing optB88 and vdW-DF. While optB88 is apparently superior in the description of dispersion in water, its description of the internal potential energy surface of the molecule is inferior enough to provide a worse performance in the fully flexible case. This is consistent with the recent calculation of McMahon, *et al.*,[58], where the structure of water from PIMD calculations with vdW-DF agree better with experiment than those obtained with PIMD and optB88. Notice that PIMD combined with vdW-DF2 produces the best overall comparison with experiment, producing an almost perfect comparison of the oxygen-oxygen pair correla-

tion function and equilibrium density. The use of frozen molecule models presents a potential limitation in the accurate description of molecular liquids, since it neglects any possible coupling between molecular vibrations and structural properties. In the case of water, this can be particularly signifiant since the liquid structure is determined by a constant competition between highly directional hydrogen bonding and anisotropic dispersion interactions. This was also suggested by McMahon, *et al.*,[58], where the balance between these two competing interactions can be shifted with the proper inclusion of nuclear quantum effects.

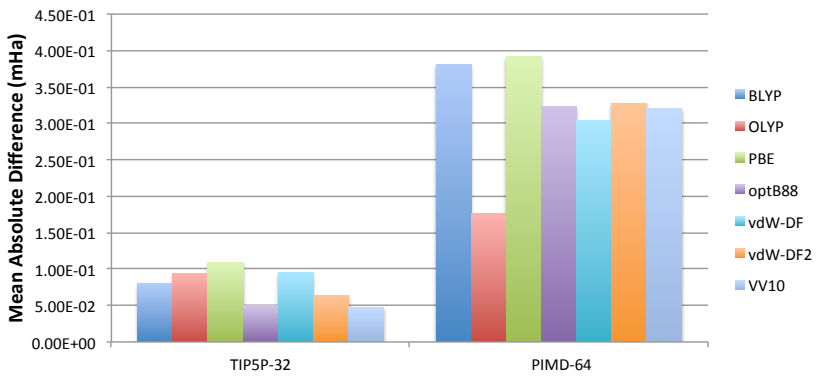

FIG. 3: (Color online) Similar to Figure 2, but the DFT calculations were performed with a USPP formulation in QE.

One surprising feature of this study came when we performed a comparison similar to that showed in Figure 2, but using QE and USPP to perform the DFT calculations. Figure 3 shows the MAD, averaged over frozen and flexible configurations, for the density functionals calculated with QE. Due to the inferior performance of QE with hybrid functionals (compared to VASP), we were not able to study any of the hybrid functionals with QE. Comparing figures 2 and 3, it is clear that the performance of some of the non-local vdW functionals is different between the two calculations. In general, both vdW-DF and vdW-DF2 perform better with QE and USPP than with VASP and PAWs, particularly in the case of frozen molecule configuration sets. In the case, vdW-DF produces results comparable to those of other GGA's, while vdW-DF2 is comparable to both optB88 and VV10. In the case of flexible molecule configurations, all vdW functionals result in a comparable performance, with vdW-DF slightly ahead of other functionals by a very small amount. The difference is produced by the use of an USPP formulation, since when either PAWs or norm-conserving pseudo potentials are used in QE we obtain results consistent both with each other and with

VASP. We currently can not explain this difference and merely limit ourselves to comparing each case separately.

In a recent ground-breaking application of Many-Body Expansions (MBE) combined with DFT and CC, Gillan, *et al.*[16,24,25] showed how CC calculations on small water clusters could be used to correct deficiencies in short-range interactions of DFT functionals in a systematic and controlled approach. The main idea of the method is to rewrite the DFT energy of the bulk system using a MBE and to substitute low order terms in the expansion with the corresponding term from CC calculations. This can be seen as a corrected DFT energy, which can be expressed as:

$$\begin{aligned} E_{DFT}^{Corr} &= E_{DFT}^{Bare} + \sum_{i=1}^{N_{mer}} (E_{CC}^{i} - E_{DFT}^{i}) \\ &= \sum_{i=1}^{N_{mer}} E_{CC}^{i} + \sum_{i=N_{mer}+1}^{\infty} E_{DFT}^{i}, \end{aligned} \tag{2}$$

where E_{DFT}^{Bare} is the original DFT energy (e.g. produced by VASP), N_{mer} represents the highest term in the expansion (e.g. dimer, trimer, etc) and $E_{CC}^{i}(E_{DFT}^{i})$ is the interaction energy corresponding to isolated clusters of size i computed with CC (DFT). The expression for the first 2 terms in the expansion are shown below:

$$E^{1} = \sum_{k}^{N} \epsilon_{k} \tag{3}$$

$$E^{2} = \frac{1}{2} \sum_{k=1}^{N} \sum_{q \neq k} (\epsilon_{k,q} - \epsilon_{k} - \epsilon_{q}) \tag{4}$$

where ϵ_k is the energy of the kth molecule, $\epsilon_{k,q}$ is the energy of the (k, q) dimer, the sum over k runs over all molecules in the unit cell and the sum over q runs, in principle, over all remaining molecules including an infinite sum over periodic images. In practice, the interaction decays quickly with distance and can be truncated at some appropriate cutoff. In this work, we choose a cutoff of 4.5 $\mathring{A}$ for both dimer and trimer terms, since we are mainly interested in showing the improvement of the correction over the studied functionals. Larger cutoffs are needed to obtain optimum improvements, in particular for the dimer term. All calculations on isolated clusters were performed with Molpro[59,61–63]. We used an aug-cc-pVQZ basis set[60] in all calculations on clusters and employed the R12 method[64] in all CCSD(T) calculations, this produced results essentially at the CBS limit for the purposes of this work.

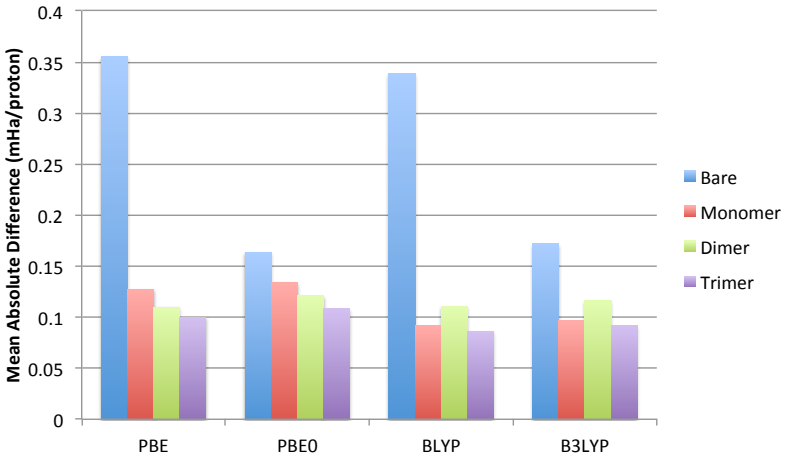

FIG. 4: (Color online) MAD of corrected DFT calculations for a selection of the DFT functionals in the vdW-DF2 configuration set.

Figure 4 shows the MAD of corrected DFT calculations for four of the DFT functionals used in this work in the vdW-DF2 configuration set. As discussed above this configuration set is dominated by the energetics associated with molecular vibrations and intramolecular interactions, where all hybrid functionals offer a drastic improvement over other functionals. In addition to the MAD of the bare DFT functional, figure 4 shows results of the MAD including corrected energies up to monomer, dimer and trimer terms. A very interesting behavior is seen in the four cases presented, for non-hybrid functionals the monomer correction is large and agrees very well with the corresponding monomer corrected hybrid functional; we choose these four functionals because they represent two pairs of functionals with similar correlation functionals and differing mainly on the inclusion of a percentage of Hartree-Fock exchange. In the case of hybrid functionals, the monomer correction is much smaller. The correction from successive terms is very small, leading to a slow convergence with expansion order. Notice that the expansion is not fully converged with respect to cluster cutoff, which leads to an even slower convergence.

While the slow convergence with cluster size can be expected because larger clusters are needed to capture long range interactions, including dispersion, the current framework offers a very promising alternative to hybrid functionals for simulations. Currently, hybrid functionals are too expensive for everyday use in ab-initio molecular dynamics simulations, requiring large scale computational resources for their use. From these results it is evident that the corrected functionals provide an equally accurate alternative, leaving only the long

range interactions described at the mean-field level, short-range interactions are described at the very accurate CC level.

IV. CONCLUSIONS

In this article we present the use of QMC calculations to benchmark the accuracy of a various exchange-correlation functionals typically used in ab-initio molecular dynamics simulations of bulk water. This provides a direct measure of the expected accuracy of DFT. Combined with a path integral representation, this allows us to minimize the approximations employed in the simulation of water and other aqueous solutions, by identifying the best functional currently available in the very large list of available ones. The comparison with QMC clearly showed the poor description of the intramolecular potential energy surface offered by non-hybrid density functionals. We also showed how the use of a correction scheme recently introduced by Gillan, *et al.*,[16], leads to a dramatic improvement in the description of the short-range interactions in the liquid, leading to non-hybrid functionals with an accuracy similar to hybrid ones. In the case of long range interactions, the proper description of dispersion interactions was shown to be important, regardless of the accuracy of the functional in the description of the short-range interactions. We found that, while optB88 seems to provide the best description of dispersion in the liquid, the vdW-DF and vdW-DF2 functionals offer the best agreement of all non-hybrid functionals when fully flexible, realistic, water configurations are considered.

To the authors' knowledge, this is the first attempt to use an accurate many-body method to benchmark mean-field approached based on DFT. While this was limited to water at ambient conditions, it presents a very promising route for the development of density functionals tailored for bulk calculations. Not only does this allows us in general to make a judgment of the quality of a functional before its use in first-principles simulations, but it also shows us a path for the systematic improvement of the functionals by adjusting free parameters to minimize the errors, e.g. the MAD. DFT users will often point to experimental data to validate the quality of a chosen functional. Water has an additional complication of using experimental data; namely because of the importance of quantum zero-point effects of the protons, fitting of the experimental data becomes particularly problematical. A common approach is to do a simulation of the classical system and assume the effective classical system

includes effects of ZPE, however this introduces a further unnecessary approximation. What we have shown is that we can use highly-accurate QMC methods as a reference, removing the need of experimental data in the construction of the functional.

While much work remains to be done in developing QMC-based finite-temperature FP methods, the calculations presented here show one possible use of accurate many-body calculations, developing DFT functionals by directly fitting points on the potential energy surface of the system from QMC. This could be seen as fitting QMC results within a DFT framework. This is an ideal combination of both approaches, offering the possibility to retain the accuracy of QMC at the mean-field cost of DFT. Combined with powerful modern clusters and the parallel nature of the problem (independent QMC calculations across the PES), this could represent a new path for many-body methods in the accurate simulation of condensed systems. Thus simulations can thereby become much more predictive, and not just produce universal properties but details important to applications and experiment. We are currently using the dataset of QMC calculations and the correction scheme based on the cluster decomposition to optimize the long range behavior of the vdW density functionals for an optimal description of bulk water. If successful, we plan to apply a similar approach for other molecular systems.

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* moralessilva2@llnl.gov

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