Editors' Suggestion

Coupled Cluster Molecular Dynamics of Condensed Phase Systems Enabled by Machine Learning Potentials: Liquid Water Benchmark

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Coupled cluster theory is a general and systematic electronic structure method, but in particular the highly accurate "gold standard" coupled cluster singles, doubles and perturbative triples, CCSD(T), can only be applied to small systems. To overcome this limitation, we introduce a framework to transfer CCSD(T) accuracy of finite molecular clusters to extended condensed phase systems using a high-dimensional neural network potential. This approach, which is automated, allows one to perform high-quality coupled cluster molecular dynamics, CCMD, as we demonstrate for liquid water including nuclear quantum effects. The machine learning strategy is very efficient, generic, can be systematically improved, and is applicable to a variety of complex systems.

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The coupled cluster (CC) method has been introduced long ago by Coester and Kümmel, dubbed "$\exp(S)$ method" at that time, to systematically tackle the many-body fermion problem in nuclear physics in a diagram-free framework that is both general and systematically improvable [1,2]. Later, the CC method has been proven to be a true game changer by granting access to highly accurate properties of small molecules and finite clusters [3]. Importantly, CC is a size-consistent theory (being termwise size extensive) and, thus, yields consistent results for systems containing different numbers of atoms. By this virtue, even truncated CC expansions allow one to accurately describe—in principle—not only molecules but also condensed phase systems, contrary to other electronic structure methods such as truncated configuration interaction (CI) which accumulate size-consistency errors for increasingly large systems. In fact, in recent years, periodic CC methods have been shown to provide highly accurate total energies of solids [4–9], albeit they are feasible only in the static ("single-point") limit and using small periodic supercells. Still, specifically the CCSD(T) method [3] has been demonstrated to yield cohesive energies of real solids surpassing an accuracy of about 0.03 eV (or 1 kcal/mol) [5].

Unfortunately, the computational cost of such CCSD(T) calculations of condensed phase systems, which explodes as a function of system size, essentially prohibits their practical use. What is missing is a generic, systematically improvable, and efficient CC-based approach that allows one to include finite temperatures and realistic structural models in conjunction with time-evolution and structural dynamics in fully atomistic simulations. These are mandatory ingredients to meaningfully describe condensed phase systems, notably liquids, in the framework of molecular dynamics. Here, we introduce such an approach, coupled cluster molecular dynamics (CCMD), and demonstrate its accuracy by computing key structural and dynamical properties of water at ambient conditions in outstanding agreement with experimental benchmark data.

Our approach is based on two ingredients. The first one is recent progress in CC methodology offering new avenues toward achieving "gold standard" quality total energy calculations of rather large yet finite molecular systems, in particular the near-linear scaling, domain-based local pair natural orbital CCSD(T), DLPNO-CCSD(T), technique [10,11]. This static method can be applied to finite molecular systems as large as those that are typically used to study liquid water using "on-the-fly" *ab initio* molecular dynamics (AIMD) simulations [12]. We recognize that these recent advances in quantum chemistry opened the door toward generating big data sets for large molecular systems that could be combined with modern machine learning (ML) potentials [13–22], which provide the second component of our framework.

Nowadays, ML potentials allow one to reach a simulation quality that was hitherto simply inaccessible for condensed phase systems such as liquid water. Indeed, rather efficient density functional theory (DFT) for periodic condensed systems has been used in the first MD simulations of flexible liquid water relying exclusively on a ML potential [23,24], employing a high-dimensional neural network potential (HDNNP) [18,25–27] in that case. Numerous other successful flavors of such ML strategies based on DFT reference data have been introduced over the years to most efficiently simulate large periodic systems, notably water, some of them even making use of ML to introduce one- and two-body corrections to DFT [28,29]. Accuracy, however, remains an issue in these cases as DFT-specific limitations are inherited [30].

For isolated molecular systems, on the other hand, it has already been demonstrated by us and others that highly accurate CCSD(T)-grade interaction potentials can be devised in a generic and automated active-learning framework upon introducing tailor-made ML strategies [31–38]. Yet, transferring CCSD(T) accuracy in a general and systematic manner to extended condensed phase simulations—liquid water being a prominent example—still remains an outstanding challenge.

In this Letter, we show how modern CCSD(T) theory of finite systems intertwined with advanced ML techniques allows one to carry out highly accurate computer simulations of condensed phase systems based on a generic and automated procedure that is applied on demand to the specific system of interest. Our active-learning ML procedure is demonstrated to parametrize a very accurate HDNNP which enables very efficient path integral coupled cluster molecular dynamics of water at ambient thermodynamic conditions, serving here merely as a particularly challenging yet exemplary target system that could be exchanged by others. Thus, our strategy is to directly generate a HDNNP that is tailor made for a specific application—rather than aiming to develop a general-purpose force field for water that is broadly transferable. In the same spirit, the approach could be applied in follow-up work to other condensed phase systems. The computational effort to simulate HDNNP bulk water at CCSD(T) accuracy is close to that of sophisticated many-body force fields—thus many orders of magnitude faster than on-the-fly *ab initio* simulations. In this context, we stress that our primary aim here is not to introduce a CCSD(T)-quality water potential as such, but rather to introduce a general computational approach that allows one to efficiently generate on demand very accurate potentials for the simulation of extended condensed phase systems, such as molecular liquids among many others, using exclusively finite-system data. Moreover, CCMD is ideally suited to use commodity single-node platforms in view of benign memory (RAM) and compute (CPU and GPU) requirements both at the training and simulation stage. Importantly, our data-driven active-learning CCMD approach is general since (i) the underlying electronic structure theory can be systematically improved, e.g., toward including strong correlation effects, and since (ii) it can be applied beyond ambient bulk water to many other types of condensed phase systems.

Key ideas and basic concept.—Current advances in computationally efficient correlated quantum chemistry allow for very accurate routine calculations of large (yet finite and static) molecular systems of ever increasing complexity [11]. In particular, the near-linear scaling DLPNO-CCSD(T) technique [10] (as available in the `ORCA` package [39]) can be applied to large molecular systems, such as finite water clusters consisting of up to about 100 molecules. It yields very high accuracy given that DLPNO-CCSD(T) has been shown to recover more than 99.9% of the full CCSD(T) correlation energy [11]. Indeed, our own validations of DLPNO-CCSD(T) against the WATER27 data set yield an average error as low as about 0.004 eV (≈0.1 kcal/mol) compared to these best benchmark data [see Supplemental Material (SM), Sec. S-I.A [40]]. Note that this is one order of magnitude lower than what is broadly called "chemical accuracy," namely 1 kcal/mol (≈0.04 eV). Within the same near-linear scaling spirit, the less accurate but computationally much more efficient DLPNO-MP2 method [84], which offers efficient analytical gradients [85], is also available. This suggests the idea of using MP2 energies and forces to construct an MP2-grade HDNNP of the system of interest at not much cost. This interim MP2-HDNNP provides the basis for an upgrade to CCSD(T) accuracy, using only energies for training, in the spirit of Δ-learning as explained in SM, Sec. S-III [40].

Machine learning strategy.—A HDNNP topology with two hidden layers containing 30 nodes each for both elements together with well-established atom-centered symmetry functions [26] is used throughout within the frame of the committee-NNP method [86,87] using eight committee members as detailed in SM, Sec. S-II.B [40]. Note that such HDNNPs provide analytical gradients and thus forces, implying that they are ideally suited to be used within MD. Having in mind the description of extended condensed phase systems subject to periodic boundary conditions, whereas the DLPNO-CCSD(T) calculations strictly require finite clusters, the long-range electrostatic as well as the short-range repulsive interactions between the atoms have been approximately parametrized and removed from the cluster energies before training the HDNNP as outlined in SM, Sec. S-II.A [40].

Another issue to tackle is the fact that is it not feasible to perform periodic CC simulations of the condensed phase target system in order to generate and improve the HDNNP, as customarily done when parametrizing ML potentials to DFT since DFT-based AIMD is easily accessible for reasonable systems sizes [12]. To solve this dilemma, our procedure gets only seeded by running standard periodic AIMD of liquid water using DFT to sample training configurations by extracting finite clusters containing 64 water molecules using farthest point sampling [88]. Similarly, we add early on DFT-based path integral configurations in order to include those crucial structural deformations in the training set that come from nuclear quantum effects where classically forbidden regions on the many-body potential energy surface are accessed. Moreover, the efficient DLPNO-MP2 method is initially used to parametrize some interim MP2-HDNNP based on these clusters while making use of consistent MP2 energies and forces [85]. The DLPNO-CCSD(T) training set configurations are selected initially using again farthest point sampling based on both, classical, and quantum nuclear

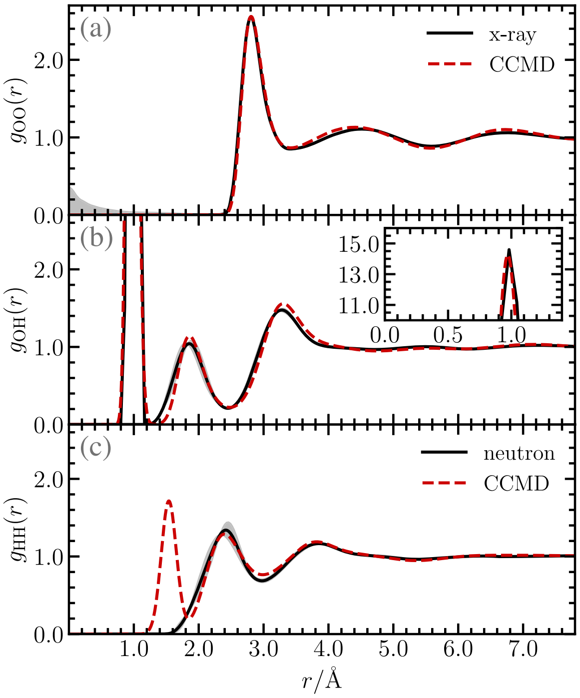

FIG. 1. Radial distribution functions of water including nuclear quantum effects from path integral CCMD simulations at 298 K (red dashed lines) compared to x-ray diffraction (a) and neutron scattering (b), (c) data (black solid lines) with their error bars (gray-shaded areas) [94,95]; see SM, Sec. S-V.A [40] for details on the presented OO RDF including information on the error bars. Only the *intramolecular* OH peak in panel (b) at ≈1 Å (that is also presented in its inset) is given by the $\Delta G_{\mathrm{OX}}(r)$ data in Fig. 2(b) obtained from O isotope substitution neutron diffraction [97] experiments at 300.6 ± 0.5 K (black solid line without error bars, digitally extracted) which approximates $g_{\mathrm{OH}}(r)$ as explained therein, whereas the intermolecular OH and HH RDFs are from [95]. The RDFs have been computed using a radial bin size of 0.01 Å as depicted and are not smoothened.

trajectories. Importantly, since any DFT-based sampling of training set configurations imposes an undesired structural bias, we switch from DFT-based sampling to using a preliminary HDNNP once it allows for numerically stable path integral simulations. Finally, the CCSD(T) accuracy of the HDNNP gets consolidated in the spirit of Δ-learning using active learning based on atomic committee force disagreement [87] of pruned path integral configurations, thus fully including the quantum nature of the nuclei directly at the CCSD(T) reference level. After validation, this systematic procedure generates the final CCSD(T)-HDNNP that is used to compute all observables while including nuclear quantum effects via dynamical path integral simulations [89]. Overall, our generic approach to CCMD simulations at CCSD(T) accuracy is schematically visualized in SM, Fig. S-4 [40] for a general condensed phase system. Clearly, all its key ingredients, i.e., the sampling of initial reference structures, the generation of the first interim MP2-HDNNP and its improvement using additional CCSD(T) energies, as well as the optimization of the final CCSD(T)-HDNNP, all based on active learning techniques, allow for a high level of automation which can be transferred to other condensed phase systems. As is well-known also in case of largely automated ML strategies, this always requires system-specific adjustments, concerning in the present case, e.g., the symmetry functions, the size of the finite clusters or when to start adding the computationally demanding CCSD(T) energies to improve upon MP2 accuracy. Toward enhancing automation, it could be interfaced in follow-up work with existing workflow software and protocols to generate ML-potentials on demand (such as e.g., `DeePMD` [90], the performance of which has actually been demonstrated for DFT-based water, to mention but one example out of many). The details on our multilevel active-learning strategy, as devised to be able to cope with computationally demanding static CCSD(T) reference calculations of finite water clusters to describe the dynamics of bulk liquid water, are described in SM, Sec. S-III [40].

Simulation methods.—We employed the `RubNNet4MD` package [91] to generate the CCSD(T)-HDNNP and the HDNNP-interface [31,92] within the `CP2k` suite [93] using its path integral module [92] to perform CCMD simulations in the framework of ring polymer molecular dynamics (RPMD) [89] to include nuclear quantum effects on both, structural and dynamical observables. Our simulations of liquid water were carried out at 298 K using 128 H_2O molecules and 32 Trotter replica. All reported properties have been obtained as averages from 50 independent CCMD RPMD runs of length 100 ps each adding up to a total statistics of 5 ns. The computational details are compiled in SM, Sec. S-IV [40].

Properties of liquid water from CCMD.—In order to judge the quality of these path integral CCMD simulations of liquid water at ambient conditions, our general strategy is to compare fundamental structural as well as dynamical quantum observables directly to properties that can be experimentally measured in a rather faithful manner. The structure of coupled cluster water as given by the three radial distribution functions (RDFs) depicted in Fig. 1 (and digitally reported, see SM, Sec. S-IV.C [40]) compares favorably to those obtained from the state-of-the-art analyses of neutron scattering and x-ray diffraction experiments [94–96] along with the intramolecular OH peak at roughly 1 Å obtained from O isotope substitution neutron diffraction [97]. Note that the earlier benchmark OO RDF of ambient water [96] features an artificial nonzero intensity for $r < 2.4$ Å which is no longer present in the RDFs of ambient water determined at several temperatures close to ambient conditions which are reported in [94]. As explained in SM, Sec. S-V.A [40], we use the latter data [94] to generate a reference $g_{\mathrm{OO}}(r)$ at 298.0 K by temperature interpolation that provides the experimental benchmark in Fig. 1(a). The agreement between the computed and experimental RDFs concerns both the heights and positions of the maxima and minima of the peaks, notably

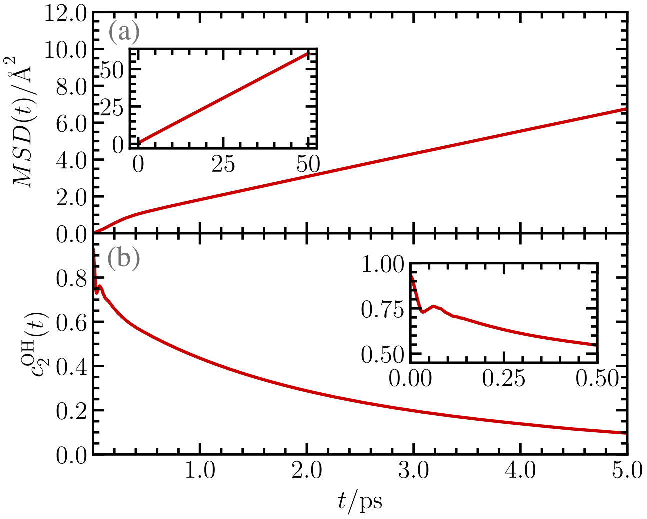

FIG. 2. Mean-square displacement (a) and C_2^{OH} orientational correlation function (b) of water including nuclear quantum effects from path integral CCMD simulations at 298 K. The insets magnify the long (a) and short (b) time behavior from zero up to 50 and 0.5 ps, respectively. The functions have been computed using a time interval of 1 fs as depicted and are not smoothened.

including the much discussed [97] first peak of $g_{\mathrm{OH}}(r)$ that stems from the covalent OH bonds in liquid water, as well as the far-ranging solvation shell modulations of liquid water including a pronounced third shell as disclosed by the OO RDF [96].

A fundamental dynamical process in liquids that can be accurately measured is the translational diffusion of individual molecules, which is closely coupled to the H-bond network dynamics in case of liquid water. The mean-square displacement in Fig. 2(a) shows a perfectly linear behavior on the relevant timescale, see inset. Based on the underlying trajectories, we compute the self-diffusion coefficient of coupled cluster water to be 0.244 ± 0.002 Å^2/ps, which is close to the recommended experimental reference value of 0.23 Å^2/ps at 298.15 K (see SM, Sec. S-V.B [40] for a discussion of this experimental value); the finite-size extrapolation of the computed observable is included and the reported error bar estimate is obtained based on 50 independent RPMD path integral simulation trajectories as detailed in SM, Sec. S-IV.D [40]. Thus, also the agreement between CCMD and experiment for this important observable that probes the structural dynamics of liquid water is very convincing.

In addition to translational motion, the orientational dynamics of water is another key dynamical process where useful experimental data are available, see SM, Sec. S-V.C [40]. Since the reorientational motion of the individual water molecules in liquid water is predominantly due to H-bond jump dynamics [98], it complements significantly the analysis of translational motion in terms of the diffusion coefficient, which is related to center-of-mass transport and thus dominated by the migration of water molecules within the fluctuating H-bond network coupled to the jump dynamics. The orientational relaxation time of the OH bond vector of coupled cluster water at 298 K turns out to be $\tau_2^{\mathrm{OH}} = 2.992 \pm 0.065$ and 1.733 ± 0.029 ps when obtained from fitting and integrating the underlying $C_2^{\mathrm{OH}}(t)$ function, respectively; see SM, Sec. S-IV.D [40] for background and note that fitted relaxation times are larger than those obtained from the integrals due to excluding the fast short-time librational decay [98]. These values are in accord with corresponding experimental reference values for ambient liquid water in the range of 1.71–1.96 ps according to NMR relaxation and 2.5–3.0 ps from IR pump-probe experiments as assessed in SM, Sec. S-V.C [40] based on detailed references.

The situation concerning the orientational relaxation as probed by the intramolecular HH vectors is more involved, but a value of about 2.5 ps is favored in an authoritative review, see SM, Sec. S-V.C [40]. We obtain $\tau_2^{\mathrm{HH}} = 3.315 \pm 0.075$ and 2.082 ± 0.037 ps for the fitted and integrated relaxation times related to the HH bond vector, respectively. Finally, the fitted and integrated molecular dipole relaxation times of coupled cluster water turn out to be $\tau_2^{\mu} = 2.823 \pm 0.121$ and 1.326 ± 0.026 ps, respectively. Here, direct comparison to experimental data is rather unclear but a value of 1.9 ps has been reported some time back for the orientational relaxation time of the dipole moment vector, see SM, Sec. S-V.C [40] for reference. Given the intricate nature of any one-to-one comparison of the computed relaxation times to experimental data [98] as addressed in SM, Sec. S-V.C [40], it is evident with reference to reliable measurements that also the underlying reorientational processes of coupled cluster water at 298 K are close to those that determine the structural dynamics of real liquid water.

Our CCMD results can also be directly compared to elaborately parametrized and highly accurate water models of the well-established truncated many-body expansion (MBE) family [99], like the most recent many-body CCSD(T) potential “q-AQUA” that includes up to four-body interactions [100], which has been published after submission of our manuscript; we refer the interested reader to SM, Sec. S-VI [40] for detailed comparisons of structural and dynamical properties of ambient water.

Status quo and perspectives.—We conclude that the highly accurate “gold standard” electronic structure method CCSD(T), applied so far to small molecules or simple solids in the static limit, has been extended to the condensed phase by intertwining it with very generally applicable machine learning techniques. The resulting coupled cluster molecular dynamics approach, CCMD, allows for finite-temperature simulations of dynamically disordered extended systems, notably molecular liquids, at CCSD(T) accuracy. Yet, the computational cost corresponds roughly to advanced force fields and, thus, is many orders of magnitude below that of respective on-the-fly *ab initio* simulations. A first proof-of-principle application to liquid water at ambient conditions demonstrates that CCMD, including nuclear quantum effects via path integrals, provides very accurate structural and dynamical properties close to the experimental benchmarks. The devised active-learning ML strategy is general, automated, and scalable to large extended systems. It can be systematically improved and applied to condensed matter other than water, thereby providing systematic access to condensed phase simulations at CCSD(T) accuracy. Finally, combining the CCMD approach with our current progress toward computing response properties, such as infrared spectra based on dipole time-correlation functions using similar ML approaches at CCSD(T) accuracy, looks very promising.

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