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Evaluating the Chemical Reactivity of DFT-Simulated Liquid Water with Hydrated Electrons via the Dual Descriptor

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ABSTRACT: Modeling the various properties of liquid water, particularly its reactivity, has been a longstanding challenge for simulation methods. Recently, *ab initio* simulations based on density functional theory (DFT) have come to the fore as tenable methods for calculating the properties and reactivity of water, with varying degrees of success for different exchange-correlation functionals. In particular, hybrid-GGA and meta-GGA functionals have been shown to reproduce many of the structural, dynamical, and energetic properties of water to a high degree of accuracy relative to their computational cost. Here, we show that the dual descriptor (DD) measure of nucleophilicity and electrophilicity, which is sometimes used to elucidate organic chemistry reaction mechanisms, can also be used to characterize the reactivity of DFT-simulated liquid water. The DD is especially apt for understanding the reactivity of excess electrons with water as its calculation explicitly involves adding and removing an excess electron from a reference system. We use the DD to explore the reactivity of water simulated using three different DFT functionals: the LDA functional (LDA), a hybrid-GGA functional (PBE0), and a hybrid meta-GGA functional (SCAN0). Using the DD, we show that the SCAN0 functional with the standard 25% Hartree−Fock exchange produces simulated liquid water with many regions that are far more reactive than either PBE0 or LDA. To understand the implications of these highly reactive regions, we then add a strong nucleophile in the form of an excess electron and find that although PBE0 and LDA predict stable hydrated electrons, the excess electron reacts nearly instantaneously with SCAN0 water via proton abstraction to form a hydrogen atom and hydroxide ion. We show that the DD provides the ability to not only predict whether or not liquid water will react with a hydrated electron but also which particular waters will be involved solely from analyzing pure water configurations generated with each functional. We rationalize this result in terms of the known trap-seeking behavior of injected hydrated electrons, which are able to find the most electronegative region in bulk water. These results highlight the utility of the dual descriptor as a fast and interpretable method for investigating condensed-phase reactivity with excess electrons.
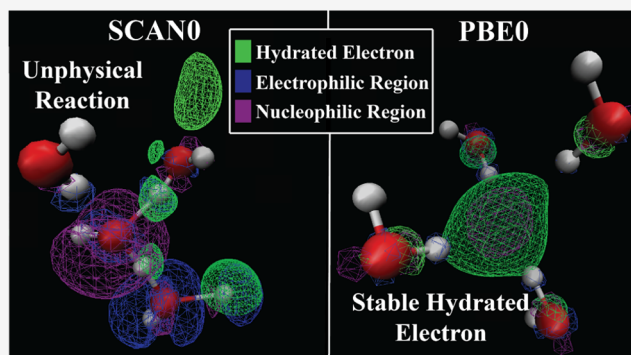
INTRODUCTION

Liquid water has long been of interest due to its central importance to living things and its many unusual properties, such as its volume expansion upon freezing, high boiling point relative to its molar mass, and ability to support a wide range of pH's. It has been challenging, however, for any simulation model of liquid water to explain all of these properties. With recent advances in computational power, however, it has become possible to simulate liquid water and aqueous solutions using *ab initio* methods, such as density functional theory (DFT).[1−6]

With advances in simulating liquid water with DFT, many groups have extended their simulations to include an excess electron, known as a hydrated electron.[7−12] Hydrated electrons play crucial roles in radiation and atmospheric chemistry,[13] and have been of considerable theoretical and experimental interest in the decades after their discovery.[14] Recently, there has been increased interest in the reactivity of hydrated electrons as potent reducing agents of organic molecules in solution.[15,16] Pairs of hydrated electrons are known to react with water to form

molecular hydrogen and hydroxide,[17−19] and we have used DFT-based simulations to examine the role hydrogen bonding plays in promoting proton transfers from water[19] as well as the spectroscopy of the various reactive intermediates.[20] Despite this, there are very few studies that directly investigate the reactivity of water simulated using different DFT exchange-correlation functionals in the presence of hydrated electrons.

In this work, we present an investigation into the reactivity of DFT-simulated water with hydrated electrons by taking advantage of the dual descriptor (DD). The dual descriptor, $\Delta f(\mathbf{r})$,[21,22] is a conceptual DFT measure that is able to highlight
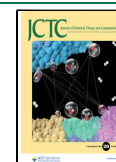
the nucleophilicity and electrophilicity of different molecular sites in a DFT-simulated system. Briefly, the DD calculates the way that the electron density ρ changes upon addition or removal of an electron from the system. Regions where $\Delta f(\mathbf{r})$ is positive represent electrophilic sites while regions where $\Delta f(\mathbf{r})$ is negative represent nucleophilic sites. The fact that calculating the dual descriptor involves changing the number of electrons in the system makes it particularly suitable for judging the reactivity of bulk water systems with an excess electron. The DD has been successful in mechanistic organic chemistry applications, where it has been able to recover the Woodard-Hoffmann rules for pericyclic reactions, rationalize the difference in reactivity of formaldehyde and ethene to nucleophiles, and recover the Markovnikov rule for electrophilic additions to asymmetric alkenes.[22]

Here, we extend use of the DD to examine reactive sites in condensed-phase systems, and in particular, the reactivity of bulk liquid water with hydrated electrons. We apply the DD to water simulated via *ab initio* DFT methods using three different exchange-correlation functionals spanning several rungs of "Jacob's Ladder,"[23] including the LDA functional (LDA),[24] a hybrid-GGA functional (PBE0),[25] and a hybrid meta-GGA functional (SCAN0).[26] Our examination of dual descriptor isosurfaces and integrated DD values around individual waters shows that SCAN0 water (with the standard 25% Hartree−Fock (H−F) exchange) is significantly more reactive than either PBE0 water or LDA water, with many more instantaneous sites that are more highly nucleophilic or electrophilic. This is interesting and slightly unexpected given that SCAN0 does a far better job at modeling the properties and structure of liquid water compared to the LDA functional.

Based on our findings with the DD, we then test the reactivity of DFT-simulated water in the presence of a hydrated electron. Hydrated electrons are experimentally known to be stable in water in the absence of protons or other hydrated electrons,[14] and have been observed to be stable for at least tens of ps in simulations using the PBE0 functional.[7,8,11,19] Our results indicate that LDA water is also capable of forming a stable hydrated electron species, but SCAN0 water is not. Instead, we find that SCAN0 water is too reactive toward an excess electron, which quickly removes a proton from a SCAN0 water molecule to form hydroxide and a hydrogen atom, a reaction that is seen experimentally at time scales ∼12 orders of magnitude longer than seen here with the SCAN0 functional. We also find that the DD shows that decreasing the amount of H−F exchange to 10% attenuates the reactivity of SCAN0 water, and indeed, when we then run trajectories with an excess electron, the proton transfer reaction no longer occurs (although we also see that the electron no longer localizes into a cavity). Thus, the way that the reactivity of SCAN0 water changes with the amount of H−F exchange provides a useful test-case for analysis with the dual descriptor.

To ensure that the nonphysical reactivity of SCAN0 water toward an excess electron was not the result of a kinetic inability to find a stable configuration, we also examined the behavior of solvated electrons in SCAN0 water both as a function of the starting configuration and as a function of the amount of H−F exchange used in the hybrid functional. We find that with >25% H−F exchange, excess electrons in SCAN0 water are stable for at most tens of femtoseconds before reacting with the water by proton abstraction. When less than 25% H−F exchange is used, the over-reactivity is attenuated although the electron remains unphysically delocalized, an observation that is predicted by the

dual descriptor. These results also highlight the usefulness of the DD to quickly identify reactivity in bulk water systems in both a visual and quantitative way. We believe that these results could generalize to systems with other solvated nucleophiles, whose reactivity would be dictated more by the fluctuations in the solvent dual descriptor near the solute rather than globally throughout the entire simulation cell.

■ METHODS

Periodic DFT-based simulations of pure liquid water with 64 water molecules were performed using the CP2K software package[27] using either the hybrid meta-GGA SCAN0,[26] hybrid-GGA PBE0,[25] or LDA[24] exchange-correlation functionals. For the hybrid functionals, the main data presented in this work used the default 25% Hartree−Fock (H−F) exchange, however tests with other amounts of exact exchange were done and are discussed in the text as well as the Supporting Information (SI). Molecular dynamics trajectories were done in the N,V,T ensemble at 298 K using a Nose-Hoover chain thermostat.[28] A time step of 0.5 fs was used and the volume of the simulation cell was chosen to reproduce the experimental density of bulk water at room temperature and pressure. Hartree−Fock exchange calculations were expedited via the auxiliary density matrix method (ADMM).[29] A triple-ζ basis set was used (TZVP-GTH) and the ADMM calculations used the cFIT3 basis. The GTH pseudopotentials used were optimized for each functional (GTH-LDA, GTH-PBE0 and GTH-SCAN). A plane wave cutoff of 500 Ry was used for the LDA and PBE0 calculations while a cutoff of 1200 Ry was used for the SCAN0 simulations. Liquid water PBE0 configurations were sampled from a single fully equilibrated 5.5 ps trajectory with 64 water molecules and periodic boundary conditions. Liquid water LDA and SCAN0 configurations were sampled from 17 and 6 ps trajectories, respectively, whose initial configurations were taken from the equilibrated PBE0 water trajectory.

DFT-based simulations of a hydrated electron with 64 water molecules were run using the same functionals and parameters as for the pure water trajectories but with the presence of an excess electron. Equilibrated PBE0 hydrated electron data was taken from our previous work,[10,11,19] amounting to ∼25 ps of *ab initio* data. We also ran trajectories where excess electrons were injected into equilibrated PBE0 and LDA water and propagated for several hundred femtoseconds as "controls" to which the reactive SCAN0 trajectories could be compared. Although the use of higher fractions of exact H−F exchange made no qualitative differences in simulated reactivity, we did see that simulations using the SCAN0 functional with less exact exchange (10%) showed qualitative differences in that an injected excess electron no longer reacted with the water. In this case, however, the excess electron quickly delocalized throughout the simulation box and never formed the type of cavity seen with the PBE0 or LDA functionals. It is possible that a localized electron might result for SCAN0 with 10% H−F exchange if a larger basis set were used, but unfortunately testing larger bases was computationally intractable for the system sizes and trajectory lengths studied here.

Since the simulated reaction of the hydrated electron to form a hydrogen atom and hydroxide is highly exothermic, a strong CSVR coupled thermostat[30] was necessary to prevent temperature divergence for the reactive SCAN0 trajectories. To test whether or not solvation kinetic barriers to producing a stable electron might be involved for the reactive SCAN0 trajectories (with ≥25% H−F exchange), we also tried several different

starting configurations for the excess electron, including that of an equilibrated PBE0 hydrated electron,[10] equilibrated SCAN[31] water containing a single chloride ion[32] with the Cl⁻ replaced by the excess electron, and equilibrated pure SCAN0 water (i.e., electron injection), as described further below. Each of these trajectories were propagated until the reaction of the SCAN0 hydrated electron with water was complete, usually within a few tens of femtoseconds. Simulations of the hydrated electron with the SCAN0 functional using only 10% H−F exchange were propagated from an equilibrated PBE0 cavity configuration for 2 ps, during which the proton abstraction reaction did not occur but the electron completely delocalized throughout the simulation box.

To quantify reactivity of the DFT-simulated water molecules with each of the three functionals, we employed the dual descriptor,[21] $\Delta f(\mathbf{r})$, to identify regions of electrophilicity and nucleophilicity in PBE0, SCAN0, and LDA pure water configurations, as well as throughout the reactive SCAN0 trajectories with the excess electron. The DD is a measure of local reactivity derived as the difference in electrophilic and nucleophilic Fukui functions:[21,22]

$$\Delta f(\mathbf{r}) = f^+(\mathbf{r}) - f^-(\mathbf{r}) \tag{1}$$

where $f^+(\mathbf{r})$ and $f^-(\mathbf{r})$ are the electrophilic and nucleophilic Fukui functions, respectively. Through the use of Maxwell relations, one can show that the dual descriptor is directly related to the second derivative of the electron density with respect to the number of electrons in the system:[22]

$$\Delta f(\mathbf{r}) = \left(\frac{\partial^2 \rho(\mathbf{r})}{\partial N^2} \right) \tag{2}$$

With this definition, regions of negative DD are preferable sites for electrophilic attack, while regions of positive DD are preferable sites for nucleophilic attack.[22] By calculating the dual descriptor for DFT-simulated liquid water, we are thus able to identify which sites are the most reactive, particularly to an injected hydrated electron, and how reactive they are. We investigated this with each of the three functionals we focus on here.

To accomplish this, for each selected simulation configuration, we performed three single-point calculations in CP2K corresponding to N, $N − 1$, and $N + 1$ electron systems (where the N-electron system corresponds to a neutral system for pure water and the singly negatively charged system for the hydrated electron). The DD[21] was then calculated from these configurations with an extra (or deficit) charge using Multiwfn[33,34] version 3.8 from the molden[35] files generated by CP2K. Processing of the dual descriptor grid data was also done with Multiwfn.[33] Plotting of isosurfaces and animation of trajectories was done in VMD.[36]

RESULTS AND DISCUSSION

To investigate the reactivity of DFT-simulated liquid water we used the dual descriptor to characterize regions of high electrophilicity and nucleophilicity. Figure 1 shows representative snapshots of the DD isosurfaces for pure liquid water simulated via DFT-based Born−Oppenheimer molecular dynamics with the PBE0 (panels a and b), SCAN0 (with the standard 25% H−F exchange, panels c and d), and LDA (panels e and f) functionals; here, blue shading represents electrophilic regions and purple shading indicates nucleophilic regions. It is immediately clear by inspection that SCAN0 water has many
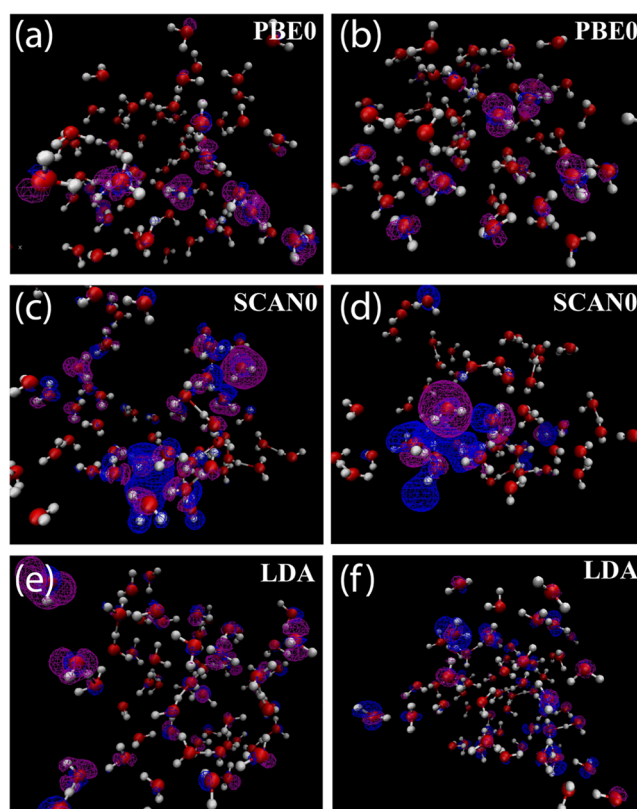

Figure 1. (a, b) Dual-descriptor (DD) (eq 1) isosurfaces for representative configurations of simulated PBE0 water, with purple representing the nucleophilic regions and blue representing electrophilic regions. Panels (c, d) show similar DD isosurfaces for representative configurations of simulated SCAN0 water (with the standard 25% H−F exchange). The isosurfaces show that SCAN0 water has a much greater prevalence of more highly reactive regions, particularly (blue) electrophilic regions on some of the water H atoms. These regions would thus be more susceptible to attack by an injected hydrated electron compared to what is seen with PBE0 water. Panels (e, f) show DD isosurfaces for LDA water, which are more similar to PBE0 water than to SCAN0.

more highly reactive regions than either PBE0 or LDA water. A brief movie visualizing how the dual descriptor changes with time as the water molecules move is given in the SI. Similar fluctuations likely occur in the first solvent shell of an atomic or molecular solute, providing a sense for reactivity with nearby electrophilic or nucleophilic water molecules.

To quantify the difference in reactivity of SCAN0, PBE0, and LDA water, we performed an analysis of the dual descriptor by integrating its value within the van der Waals radii of the water O and H atoms; we also integrated the DD over the entire system, with ensemble-averaged results summarized in Table 1. Here, more negative values indicate more nucleophilic atoms while less negative or positive values indicate more electrophilic atoms. We also examined the minimum and maximum DD values for O and H atoms in each water configuration for all three DFT functionals.

Although the magnitude of the dual descriptor is roughly similar for all three DFT functionals, the data show that SCAN0 with the standard 25% H−F exchange produces more extreme values of the DD (both the average minimum and average maximum values around each atom) compared to PBE0 or LDA. This shows that there is a much higher variation in reactivity for SCAN0 water with fluctuations much greater than for the other

Table 1. Statistics of the Integrated Dual Descriptor (DD, Eq 1) around O and H Atoms of PBE0-, SCAN0-, and LDA-Propagated Liquid Water Configurations Calculated Using the Same Functional as Used for the Propagation[a]

propagation functional	DD functional	atom	min DD (1×10^{-2})	max DD (1×10^{-2})	mean DD (1×10^{-2})	total (1×10^{-2})
				dual descriptor statistics		
PBE0	PBE0	O	-4.1 ± 0.5	1.34 ± 0.15	-0.062 ± 0.025	-24 ± 2.2
		H	-1.7 ± 0.4	0.72 ± 0.11	-0.007 ± 0.017	
PBE0	SCAN0	O	-12 ± 8	8.4 ± 2.9	0.0 ± 0.18	-2 ± 6
		H	-11 ± 9	8.1 ± 3.1	0 ± 12	
SCAN0	SCAN0	O	-15 ± 6	4.5 ± 1.2	-0.15 ± 0.13	36 ± 13
		H	-6 ± 4	3.1 ± 0.9	-0.01 ± 0.07	
SCAN0	PBE0	O	-4.5 ± 0.5	1.45 ± 0.17	-0.034 ± 0.028	11.3 ± 3.4
		H	-3 ± 0.5	1.03 ± 0.14	-0.006 ± 0.018	
LDA	LDA	O	-1.7 ± 0.7	1.23 ± 0.16	0.053 ± 0.015	12.5 ± 2.6
		H	-0.7 ± 0.4	0.63 ± 0.08	0.029 ± 0.008	

[a]Averaging was done over 8 independent PBE0 configurations, 13 independent SCAN0 configurations, and 8 independent LDA configurations. SCAN0 with the standard 25% H−F exchange tends to generate O and H atoms with more extreme values of the dual descriptor, suggesting a higher tendency for reactivity with injected hydrated electrons. Both PBE0 and SCAN0 have nucleophilic mean DD's, however SCAN0 has a much larger spread of these values. LDA shows a weakly electrophilic mean DD, with a spread closer to that of PBE0. PBE0 and LDA both generate structures with more moderate reactivity than SCAN0, with PBE0 creating more nucleophilic O and H atoms compared to LDA. PBE0 and LDA give moderately negative and positive total DD's respectively, while SCAN0 gives a large, positive total DD with a large deviation.

two functionals, verifying the conclusions from our visual inspection of configurations in Figure 1. The average values of the dual descriptor on the H atoms are only mildly nucleophilic for PBE0 and mildly electrophilic for LDA, while SCAN0 H atoms have both a more nucleophilic average value and a much larger standard deviation, again indicating both increased average reactivity and a higher sensitivity to fluctuations of the system.

When examining the total integrated dual descriptor over the entire water system, we see that both SCAN0 and LDA give positive (net electrophilic) values, with SCAN0's average integrated DD value being three times more electrophilic with a six times larger standard deviation. PBE0 water, in contrast, has a negative (net nucleophilic) average total integrated DD, with a standard deviation comparable to LDA. We will show below that the larger DD fluctuations with SCAN0 water with the standard 25% H−F exchange lead to unphysical reactivity with an injected hydrated electron compared to LDA and PBE0 water.

Unfortunately, the above analysis does not tell us whether the greater DD-predicted reactivity of SCAN0 water results from the fact that the water molecules have a different average configuration than PBE0 or LDA water,[1,3−5] or if the difference reflects something intrinsic about the reactive nature of the functionals. To test this, we ran a cross-analysis where we took water configurations generated with one functional and then calculated the DD using a different functional. We then analyzed the results in the same way as above, examining average and extreme DD values over all O and H atoms as well as the integrated DD of the entire system. These results, where the "propagation functional" differs from the "DD functional", are also summarized in Table 1.

This cross-analysis shows that when the SCAN0 functional with the standard 25% H−F exchange is used to calculate the DD for PBE0 water configurations, the minimum and maximum DD values become more extreme and the deviation of these quantities becomes larger. The total integrated DD goes from being quite nucleophilic to being weakly nucleophilic and even potentially electrophilic within the uncertainty. We see the opposite trend when we use the PBE0 functional to calculate the DD for SCAN0 water configurations, where the atom-centered DD quantities become less extreme with smaller deviations, and

the total integrated DD also becomes much less electrophilic. This leads to the conclusion that SCAN0 water is more reactive than PBE0 (and also LDA) water due to the inherent properties of the functional and not because of differences in the water structure produced by the different functionals. In the SI, we show the results of a cross-analysis where the DD was calculated using SCAN0 with 10% H−F exchange on configurations propagated from SCAN0 with 25% exchange. Both the total integrated DD as well as the integrated values around individual O and H atoms show that 10%-exchange SCAN0 functional has reduced nucleophilicity, more in line with the reactive character of LDA (see Figures S2−S4).

To determine which DFT functional better describes the chemical reactivity of liquid water with an injected excess electron and what DD values correspond to unphysical reactivity, we added an extra electron into each of our DFT simulations of liquid water. The hydrated electron is known to be a powerful nucleophile, and indeed hydrated electrons can abstract protons from liquid water, although the rate of this reaction is quite slow.[37,38] Thus, hydrated electrons should be completely stable in liquid water on the time scales accessible via *ab initio* MD simulations. Our DD analysis of the pure water configurations suggests that PBE0, SCAN0, and LDA water should show different propensities for reactivity with hydrated electrons. This is because hydrated electrons injected into the conduction band are able to experience the entire simulation cell and thus find the most electrophilic regions available in which to localize. Indeed, injected hydrated electrons have been shown to be trap-seeking in nature rather than trap-digging.[39,40]

Previous work from our group[10,11,41] as well as others[7,8] has used the PBE0 functional to simulate hydrated electrons. These simulations have shown that the excess electron localizes into a stable cavity surrounded by ∼5 water molecules that strongly donate H-bonds to the electron. We note that this "cavity" behavior of the hydrated electron is currently the most common solvation structure promoted in the literature. In the past, our group has advocated for a noncavity model of the hydrated electron,[42−45] although it has become increasingly clear that a cavity model of the hydrated electron is more consistent with many of the experimental observables for this object.[46−48] With that said, we note that many of the details of the solvation
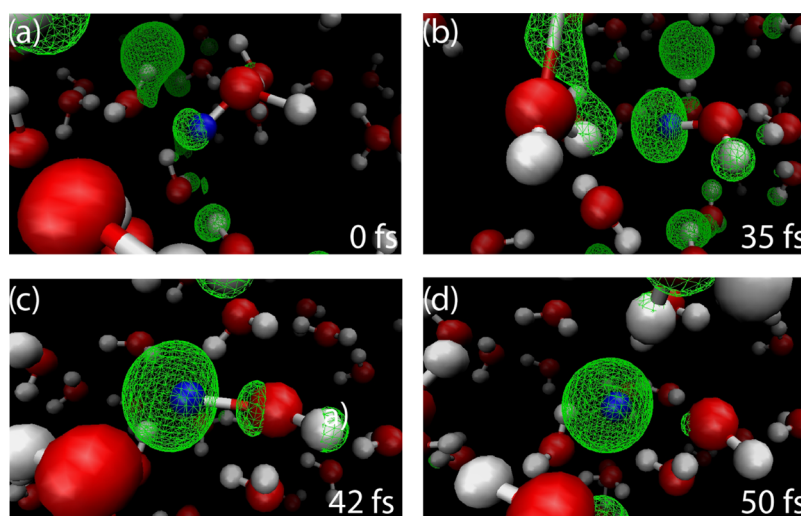
Figure 2. (a−d) Snapshots of a SCAN0 (with 25% H−F exchange) propagated trajectory showing the reaction of an excess electron injected at $t = 0$ with one of the water molecules to form an H atom and hydroxide. The green isosurface shows the spin density of the excess electron while red spheres represent O atoms and gray spheres represent H atoms. Only the atoms closest to the reactive proton (which is colored blue) are shown for clarity. The injected electron is largely delocalized among the waters throughout the simulation box, however a small region with enhanced spin density is drawn toward a reactive H atom on a neighboring water molecule. The electron quickly envelopes the proton and rapidly abstracts it from the water, forming an H atom and hydroxide. The newly formed hydroxide ion then rapidly interchanges identity with neighboring waters via proton transfer, a form of "hopping" that is well-known for this species and is shown in more detail below in Figure 4.[54]

structure of the hydrated electron are still the subject of debate in the literature.[8,10,11,19,42,49]

DFT-based simulations using the PBE0 functional have been able to explain the slope of the temperature dependence of the hydrated electron's absorption spectrum,[9] although the absolute position of the calculated spectrum is off by ≥400 meV and the spectral shape is also incorrect.[9,10] We have argued previously that the hydration environment around the PBE0 electron is overstructured, thus leading to incorrect predictions for ion-pairing between the electron and Na^+,[11] the electron's partial molar volume,[12] and the homogeneity of the electron's absorption spectrum.[41] It is worth noting that our group used the PBE0 functional with the default 25% H−F exchange for simulating the hydrated electron,[10−12,19,20] while other groups have used 40% H−F exchange to better match the experimental band gap of liquid water,[7] but the results with the two different amounts of H−F exchange are very similar.

To our knowledge, neither the SCAN0 nor LDA functionals have been used to simulate hydrated electrons via DFT. Our DD analysis suggests that LDA water has a similar magnitude of reactivity compared to PBE0 water but with a slightly more nucleophilic nature, whereas SCAN0 water should be more electrophilic and thus potentially more reactive toward an excess electron. Thus, exploring the use of the SCAN0 and LDA functionals for the hydrated electron provides an excellent test as to whether the magnitude or sign of the DD is more important for describing the reactivity of liquid water with injected hydrated electrons.

Upon injection of an excess electron into SCAN0 water, we find that the excess electron is initially delocalized across most of the simulation cell. But unlike what has been seen with other functionals,[7,50] instead of dynamically coalescing into a single localized cavity, the SCAN0 hydrated electron always remained delocalized until it reacted with a water molecule (after only a few tens of fs following injection) to form hydroxide and a hydrogen atom; the SI shows a movie visualizing this reaction from one of our trajectories. We also found that lowering the

percent of H−F exchange to 10%[51] does seem to attenuate the over-reactivity of SCAN0, but still yields a completely delocalized hydrated electron that never coalesces into a cavity (see the SI for further details).

Figure 2 shows several snapshots along a representative SCAN0 hydrated electron trajectory, with the spin density of the excess electron shown as the green mesh surface and the proton that is abstracted shown in blue. The only reactions of excess electrons in liquid water that are known to occur on time scales this fast are when electrons react with excess protons to form H atoms and water,[52] and when two hydrated electrons simultaneously react with two water molecules for form H_2 and two OH^- ions.[17−20,53] Thus, the rapid reaction of the electron with SCAN0 (with 25% H−F exchange) water in the absence of an excess proton or a second hydrated electron is nonphysical.

When excess electrons are injected into liquid water, they have more reducing power while they are delocalized than after they become equilibrated hydrated electrons,[8] so we thought it might be possible that the SCAN0 hydrated electron could become stable if it were pre-equilibrated. To test this idea, we ran SCAN0 (with 25% H−F exchange) water AIMD trajectories with an excess electron from two sets of additional initial configurations. First, we took equilibrated PBE0 hydrated electron configurations from our previous work,[10,11] and second, we took equilibrated configurations from a simulation of SCAN water containing a single chloride ion with the Cl^- removed.[32] Each of these scenarios has a pre-existing water cavity that should be suitable for stabilizing a hydrated electron.

In all of our SCAN0 hydrated electron simulations, however, no matter what the initial configuration, we saw that an H-atom abstraction reaction between the electron and SCAN0 water occurred quickly, within 50 fs when the default 25% H−F exchange was used; the reaction time extended to up to 200 fs when the amount of H−F exchange was increased, as described in more detail in the SI. As mentioned above, decreasing the amount of H−F exchange to 10% shuts off the rapid proton

abstraction reaction, but still yields a delocalized electron that never coalesces into a localized object. Thus, the net conclusion is that SCAN0 water (with ≥25% HF exchange) is much too reactive toward excess electrons, independent of the initial configuration.

We next examined the mechanism of the excess electron's proton abstraction reaction in SCAN0 water. We found that immediately following the formation of the H atom, there was a rapid series of proton transfers involving the hydroxide ion product, so that the hydroxide quickly ends up a few solvent molecules away from the water that initially lost its proton, as discussed further below. This type of proton "hopping" is commonly seen in quantum simulations of excess protons and hydroxide in aqueous solution,[54,55] as well as in reactions of dielectrons with water,[19] although here the proton migration takes place following an unphysical chemical reaction. We note that although it has not published in the archival literature, a similar reaction has been seen in DFT-based simulations of the hydrated electron using the BLYP functional.[50] The fact that we see the same reaction here despite the use of pre-equilibrated starting configurations suggests that there is something intrinsic to certain DFT functionals that makes their description of liquid water too reactive.

To better understand the extra reactivity of SCAN0 water toward the hydrated electron in comparison to the other functionals, we integrated the amount of spin density around each water oxygen atom immediately following addition of an excess electron. The resulting spin density distributions were then ensemble-averaged over the initial frames of 8 PBE0, 13 SCAN0, and 8 LDA electron injection trajectories, with the results shown in Figure 3. In this figure, the percent of the
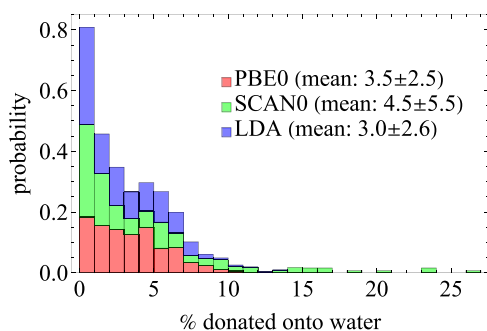

Figure 3. Histogram distributions of the percent of the excess electron's spin density that resides on individual water molecules immediately upon injection into PBE0 (red), SCAN0 with 25% H−F exchange (green), and LDA (blue) water. Though each functional sees an average donation of only a few percent of the hydrated electron's density onto waters following injection, the spread of these distributions is quite different. PBE0 and LDA water show much tighter spreads of charge donation, indicating that most waters see only a small amount of the excess electron prior to localization. SCAN0 has a distribution with a very long tail, indicating that some waters see a significant fraction of the excess electron and are therefore primed to quickly react.

electron density on the abscissa is the total spin density around a single water divided by the total integrated spin density for that configuration, so that 0% represents a configuration where the electron is completely between all of the water molecules and 100% would mean that the electron resides entirely on a single water molecule, effectively forming a water anion.

Figure 3 shows that, on average, an injected electron in SCAN0 water has roughly ~4.5% of its spin density residing on

water molecules, whereas electrons injected into PBE0 and LDA water had only ~3.5 and ~3.0% of their spin density on water, respectively. Moreover, the distribution of the amount of excess electron spin density donated onto waters is narrower for PBE0 and LDA water (standard deviation of ~2.5 and ~2.6%, respectively) than for SCAN0 (standard deviation of ~5.5%). This indicates that there are always, on average, a few SCAN0 water molecules where the excess electron places considerable spin density. This fits well with the DD examined in Figure 1, which shows that SCAN0 configurations with 64 waters always have at least a few waters with very highly electrophilic H atoms; it is these waters that tend to immediately capture part of an injected electron's spin density, quickly leading to reaction, a result that makes sense given the known overlocalization of SCAN0 with amounts of H−F exchange exceeding 25%.[51] We note that Figure S5 shows that reducing the amount of H−F exchange to 10% also attenuates this significant donation of spin density onto waters displayed by SCAN0 with 25% exchange.

To understand more about what drives this reactive SCAN0 water chemistry, Figure 4 shows snapshots of a reactive trajectory (similar to Figure 2), but also showing isosurfaces of the DD (blue for electrophilic regions and purple for
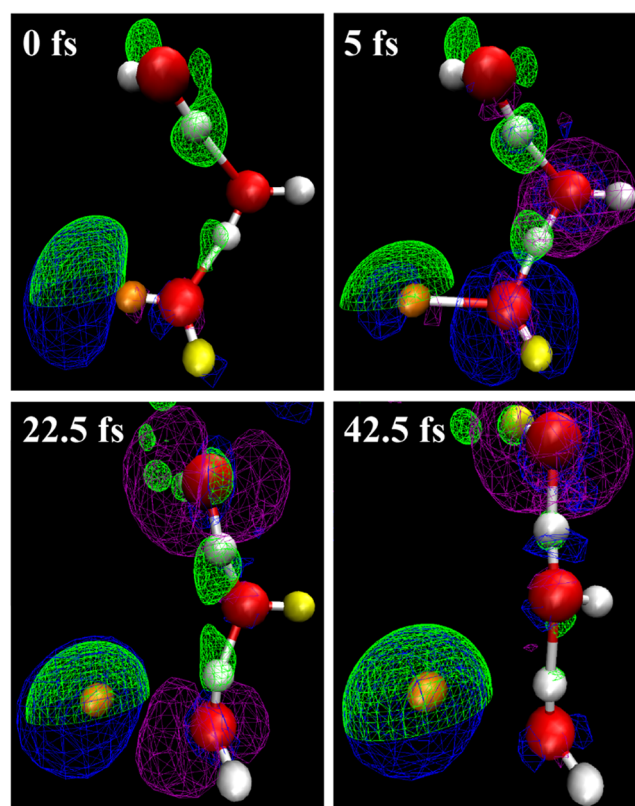

Figure 4. Snapshots from a representative reactive SCAN0 (with 25% H−F exchange) hydrated electron trajectory. The green mesh isosurface represents the excess electron (cf. Figure 2) while the blue and purple surfaces represent the electrophilic and nucleophilic regions of the dual descriptor (cf. Figure 1), respectively. Clearly, the proton abstraction takes place from the most electrophilic hydrogen in the box (colored orange), followed by concerted transfer of the identity of the resulting hydroxide via an H-bond chain (H atom on hydroxide colored yellow). The reaction is rapid because the appearance of highly electrophilic regions is controlled by water librations (see the SI) and because the electron is highly delocalized. For clarity, water molecules not directly involved in the reaction of the H-bond chain are hidden.

nucleophilic regions, as in Figure 1) along with the excess electron (shown in green as in Figure 2). These snapshots show that the electron is able to quickly find the most electrophilic H atom that is involved in a local H-bond chain. After this electrophilic proton is abstracted, the identity of the hydroxide product is rapidly exchanged down the H-bond chain (yellow H), similar to what is seen in the first step of the reaction of dielectrons with water,[19,20] while the abstracted proton (here shown in orange) remains as a neutral H atom.

The fact that the reaction takes only a few tens of fs makes sense, as the fluctuations in electrophilicity and nucleophilicity of SCAN0 water as measured by the DD take place on this time scale as they are driven by water librations; as mentioned above, there is a movie showing the dynamics of the DD in the SI. Thus, the delocalized excess electron only has to wait roughly a water librational period for a highly electrophilic H atom in an H-bond chain to appear near a region of high electron density, so the proton abstraction reaction in SCAN0 water is quite facile. We believe that similar DD fluctuations would take place in the solvation shells of molecular solutes, providing a way to understand the reactivity of other nucleophiles or electrophiles in DFT-simulated liquid water or other solution-phase systems.

As mentioned above, DFT is not a systematically improvable theory, so that simulations of hydrated electrons need to be independently benchmarked in order to understand how they depend on the particular DFT functional being used. The DD allows us to do exactly this without the need for running explicit hydrated electron trajectories, providing a significant degree of computational savings. Using the DD, we have uncovered the fact that the high level hybrid meta-GGA SCAN0 functional, when certain amounts of exact exchange are used, shows unphysical over-reactivity with excess electrons simply by sampling pure water configurations. Furthermore, the DD was able to distinguish that PBE0 and LDA water are less reactive than SCAN0 water and thus more able to localize a stable hydrated electron. Thus, the DD can aid in both qualitatively and quantitatively analyzing the reactivity of condensed-phase systems with injected hydrated electrons and potentially other solutes with different exchange-correlation functionals in DFT-based *ab initio* MD simulations.

CONCLUSIONS

In summary, we have investigated the reactivity of DFT-simulated liquid water with injected hydrated electrons using the LDA functional, a hybrid-GGA functional (PBE0), and a hybrid meta-GGA functional (SCAN0), using the dual descriptor. We find that, no matter where the water configuration comes from, the SCAN0 functional with $\geq$25% H$-$F exchange produces some water molecules with too high a degree of reactivity. When we then introduced an excess electron into these simulations of liquid water, we found that SCAN0 water reacted essentially immediately with the electron, rapidly breaking a water O$-$H bond to form a neutral hydrogen atom and a hydroxide ion, and the water that reacts with the electron is the one identified by the DD as being the most electrophilic. This unphysical reactivity of SCAN0 water was seen independent of the starting configuration. The DD also showed that lowering the amount of exact exchange to 10% reduces this over-reactivity, and indeed we saw that with the lowered amount of H$-$F exchange, SCAN0 water no longer reacted with an excess electron, although the electron remained unphysically delocalized. This work highlights the utility of the DD in being able to predict the both extent and site of condensed-phase reactivity with hydrated electrons without

actually having to run a reactive trajectory, providing a significant computational advantage.

We believe that use of the DD could potentially generalize to reactive systems with other nucleophiles, although unlike with injected electrons, most reactive molecules are localized to a particular region of the bulk solution and only move via diffusion. For this case, fluctuations of the dual descriptor in the vicinity of the solute would be more important than examining the global nature reactive sites, as molecular solutes must wait for a fluctuation to bring a reactive region into the first solvent shell.

We close by noting that our simulations do not account for nuclear quantum effects (NQEs), which can be particularly important for simulations of bulk water.[56] Although including NQEs into our simulations could change the types of water configurations sampled during pure water molecular dynamics propagation, our results showed that the functional used to calculate the dual descriptor matters more than details of the molecular configuration. Thus, we expect that the reactivity trends illuminated by the DD would be qualitatively the same with or without NQEs. Overall, this work highlights the use of using the dual descriptor to investigate chemical reactivity (in addition to structural and dynamical properties) when evaluating the performance of a particular exchange-correlation functional for simulating hydrated electrons and possibly other reactive solutes with DFT.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jctc.4c00580.

> Calculations and the SCAN0 reactive trajectories (PDF)

> SCAN0 hydrated electron always remained delocalized until it reacted with a water molecule to form hydroxide and a hydrogen atom (MP4)

> Dual descriptor changes with time as the water molecules move (MP4)

> PBE0 hydrated electron initial configuration (MP4)

> SCAN0 hydrated electron rapidly reacting with water (MP4)

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Notes

The authors declare no competing financial interest.

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