

Evaluating Simple *Ab Initio* Models of the Hydrated Electron: The Role of Dynamical Fluctuations

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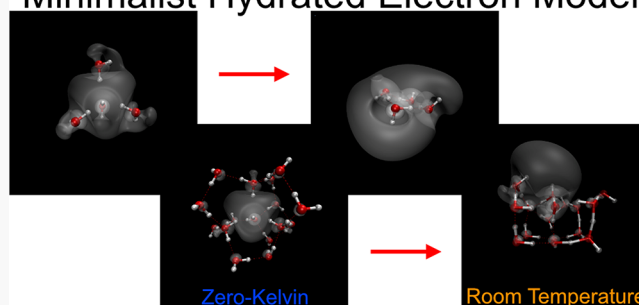
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ABSTRACT: Despite its importance in electron transfer reactions and radiation chemistry, there has been disagreement over the fundamental nature of the hydrated electron, such as whether or not it resides in a cavity. Mixed quantum/classical simulations of the hydrated electron give different structures depending on the pseudopotential employed, and *ab initio* models of computational necessity use small numbers of water molecules and/or provide insufficient statistics to compare to experimental observables. A few years ago, Kumar et al. (*J. Phys. Chem. A* 2015, 119, 9148) proposed a minimalist *ab initio* model of the hydrated electron with only a small number of explicitly treated water molecules plus a polarizable continuum model (PCM). They found that the optimized geometry had four waters arranged tetrahedrally around a central cavity, and that the calculated vertical detachment energy and radius of gyration agreed well with experiment, results that were largely independent of the level of theory employed. The model, however, is based on a fixed structure at 0 K and does not explicitly incorporate entropic contributions or the thermal fluctuations that should be associated with the room-temperature hydrated electron. Thus, in this paper, we extend the model of Kumar et al. by running Born–Oppenheimer molecular dynamics (BOMD) of a small number of water molecules with an excess electron plus PCM at room temperature. We find that when thermal fluctuations are introduced, the level of theory chosen becomes critical enough when only four waters are used that one of the waters dissociates from the cluster with certain density functionals. Moreover, even with an optimally tuned range-separated hybrid functional, at room temperature the tetrahedral orientation of the 0 K first-shell waters is entirely lost and the central cavity collapses, a process driven by the fact that the explicit water molecules prefer to make H-bonds with each other more than with the excess electron. The resulting average structure is quite similar to that produced by a noncavity mixed quantum/classical model, so that the minimalist 4-water BOMD models suffer from problems similar to those of noncavity models, such as predicting the wrong sign of the hydrated electron’s molar solvation volume. We also performed BOMD with 16 explicit water molecules plus an extra electron and PCM. We find that the inclusion of an entire second solvation shell of explicit water leads to little change in the outcome from when only four waters were used. In fact, the 16-water simulations behave much like those of water cluster anions, in which the electron localizes at the cluster surface, showing that PCM is not acceptable for use in minimalist models to describe the behavior of the bulk hydrated electron. For both the 4- and 16-water models, we investigate how the introduction of thermal motions alters the predicted absorption spectrum, vertical detachment energy, and resonance Raman spectrum of the simulated hydrated electron. We also present a set of structural criteria that can be used to numerically determine how cavity-like (or not) a particular hydrated electron model is. All of the results emphasize that the hydrated electron is a statistical object whose properties are inadequately captured using only a small number of explicit waters, and that a proper treatment of thermal fluctuations is critical to understanding the hydrated electron’s chemical and physical behavior.

Minimalist Hydrated Electron Model



INTRODUCTION

The hydrated electron is one of the simplest possible condensed-phase quantum mechanical systems, consisting of an excess electron solvated by water molecules. Hydrated electrons play an important role in chemical reactions such as ionization and electron transfer as well as in radiation chemistry.^{1–3} Despite their importance, there are still a number of unanswered questions concerning basic features of hydrated electrons, such as the local structure of the water

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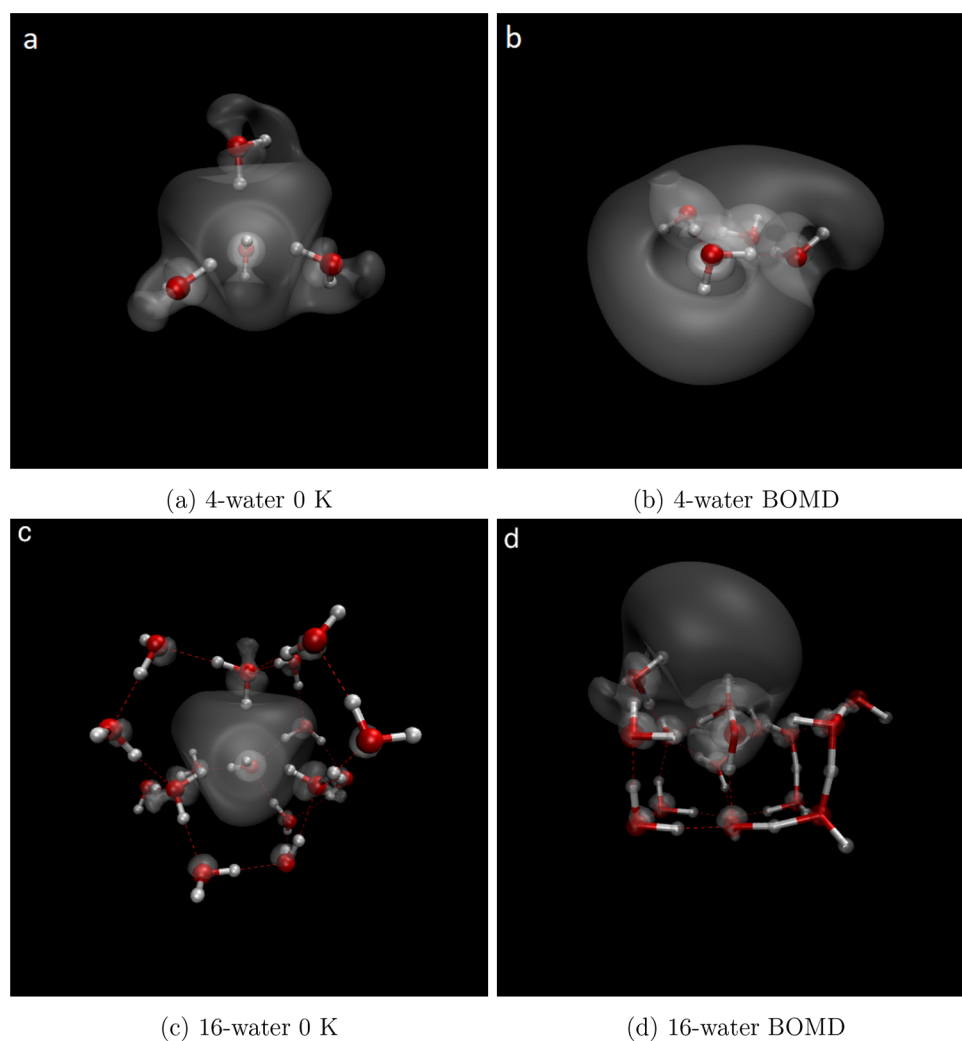


Figure 1. (a) Four-water + PCM, 0 K, tetrahedral hydrated electron geometry of Kumar et al.,¹² optimized using the BNL functional. The optimization was done by applying geometric constraints to ensure a tetrahedral water geometry. (b) A representative snapshot from the room-temperature BNL-based 4-water BOMD trajectories. (c) The BNL-optimized 16-water + PCM, 0 K, tetrahedral hydrated electron geometry of Kumar et al. (d) A representative snapshot from the room-temperature BNL-based BOMD trajectories using 16 water molecules. For all four panels, the gray surface represents the 70% contour of the spin density. Clearly, the initially tetrahedral 0 K geometry surrounding the excess electron changes drastically when dynamics are applied, with the waters favoring hydrogen bonding to each other more than with the excess electron. Thermal motions also cause the excess electron density to move outward in a fashion not seen at 0 K, emphasizing the importance of fluctuations in determining the hydrated electron's structure.

molecules that stabilize the excess charge. There is strong evidence suggesting that hydrated electrons have little occupancy in the water molecular orbitals, so that the majority of their charge density lies primarily between the water molecules in the bulk liquid.^{4,5} However, the manner in which water reorganizes around an excess electron and the details of the corresponding electronic structure are still the subject of a great deal of debate.

The standard structural picture developed over the years is that the excess electrons occupy a cavity in the water, locally expelling water from a volume midway in size between a chloride and bromide ion. This picture was supported by both early mixed quantum/classical MD simulations^{6–10} as well as by more recent *ab initio* simulations,^{11–15} although we note that some of these simulations present only snapshots,¹⁴ and others present pair distribution functions without other ways of characterizing the hydrated electron's structure.^{11,13,15} Other simulations, however, have suggested that the excess electron contains a significant number of interior water molecules,¹⁶ so

that its charge density has significant overlap with the surrounding water. We note that significant overlap of the electron's spin density with the surrounding water, an idea that is supported by EPR experiments,^{17,18} also occurs in some simulations in which the electron does have a central cavity.^{4,11}

Part of the reason for the controversy is that different structural models of the hydrated electron predict observables that agree with experiment about equally well, or equally poorly, depending on the experiment in question. Nearly every model is able to correctly predict the hydrated electron's room-temperature absorption spectrum,^{7,9,16,19} which is directly related to its radius of gyration.²⁰ Simulation models that predict that the electron resides in a cavity are also usually able to correctly predict the hydrated electron's molar solvation volume,^{21,22} and some are also able to predict the resonance Raman spectrum,²³ but most fail (or never attempt) to reproduce the temperature dependence of the electron's absorption spectrum,²⁴ excited-state lifetime,^{25,26} the fact that the electron's absorption spectrum is homogeneously

broadened,^{27,28} or the experimentally measured time-resolved photoelectron spectroscopy (TRPES).²⁹ Noncavity simulation models, on the other hand, reproduce the temperature-dependent properties, the homogeneity of the absorption spectrum, and the TRPES and behavior of the hydrated electron near interfaces well^{21,25,26,29} but predict the wrong sign for the molar solvation volume as well as miss (depending on the level of theory) the resonance Raman experiments.^{21,23,30} Also, unfortunately, of the few fully *ab initio* models that have been explored, the computational expense is so high that it is nearly impossible to include enough water molecules or to produce enough statistics to provide meaningful comparisons with any of the above experiments.^{13–15}

A few years ago, Kumar et al. proposed a simple density functional theory (DFT)-based *ab initio* model of the hydrated electron consisting of only four quantum mechanical water molecules plus an excess electron surrounded by a polarizable continuum (PCM).¹² The idea of using only four water molecules came from starting with the initial octahedral cavity structure proposed by Kevan,³¹ which was found to optimize into a locally tetrahedral cavity structure around the excess electron regardless of the calculation method of choice. These workers also explored the use of an additional explicit solvation shell, with a total of 16 water molecules plus PCM, and saw no change to the basic tetrahedral cavity structure, suggesting that this simple tetrahedral model correctly captures the quantum mechanical essence of the hydrated electron largely independent of the DFT functional used.¹² The 0 K tetrahedral structure seen by Kumar et al., shown in Figure 1a, is indeed reminiscent of that seen in many traditional cavity model simulations but has more overlap of the electron's charge density with the explicitly treated waters than most such models.¹²

After optimizing the geometry of their 4- and 16-water molecule systems to obtain a tetrahedral cavity structure, Kumar et al. then tuned the size of the central tetrahedral cavity in order to explore the relationship between the cavity size and the experimental vertical detachment energy (VDE) of the hydrated electron.^{12,32–35} This simplistic 0 K model performed remarkably well when compared to a diverse set of experimental observables, including the room-temperature thermodynamic properties, suggesting that the hydrated electron indeed has a single average structure that seems to be dominant at room temperature. This model also has been used to explore the reduction of the DNA bases.³⁶ We were surprised that a static model could correctly represent the room-temperature fluctuating object, which is why, in this work, we extend the Kumar et al. hydrated electron model by using it as a basis for Born–Oppenheimer molecular dynamics (BOMD), so that entropic effects are explicitly accounted for. Because the model is relatively inexpensive, having either only 4 or 16 quantum mechanically treated waters, we are able to run long trajectories (tens to hundreds of ps duration) and to test the model using different DFT functionals. In this way, we can understand the effects of thermal motions and fluctuations on the properties of this minimalistic *ab initio* model of the hydrated electron. We are also able to run the simulations with an optimally tuned range-separated hybrid functional, which provides a significant advance over other DFT-based simulations that use more standard hybrid functionals.^{11–13,15}

For the minimalist 4-water BOMD model of the hydrated electron, we find that when dynamics and thermal motions are

introduced to the system, the excess electron is not effectively confined by the four water molecules and PCM but instead oozes out away from the explicit waters. The initial tetrahedral arrangement of the four water molecules is also destroyed by thermal motions, with the positions of the four waters becoming highly fluxional. Moreover, the average geometry for this model near room temperature exhibits a planar arrangement of water molecules reminiscent of the gas-phase water tetramer, emphasizing how important dynamics and fluctuations are to the hydrated electron system. We also find that the average structure of this simple *ab initio* BOMD model more closely resembles previous noncavity models rather than the traditional cavity model, and thus, this model suffers from all the same problems as noncavity models. We introduce a set of structural parameters that can be used to numerically quantify how cavity-like (or not) a particular hydrated electron model is. Finally, we calculate the simulated steady-state absorption spectra, photoelectron spectrum, and resonance Raman spectra of the model and show that the thermally fluctuating structures do indeed behave somewhat similarly to the experimental hydrated electron, although there is significant deviation due to the fact that the 4-water system overly fluctuates.

We then extended the model with 12 additional explicit water molecules to serve as a second solvation shell. We find, however, that the local structure of the electron is basically the same as what we observed with only four explicit waters: the electron has little direct interaction with the majority of the additional explicit waters. In fact, the results of our 16-water BOMD trajectories strongly resemble those run without PCM to simulate small water anion clusters,³⁷ with the excess electron preferring to reside at the cluster surface (where it is stabilized by H-bonds) rather than in the cluster interior. This means that PCM cannot be used as a substitute for explicit waters when considering the properties of the hydrated electron. All of the results suggest that the bulk hydrated electron is a statistical object that requires the interaction of many waters, likely hundreds, in order to correctly describe its experimental properties. The use of small numbers (i.e., tens of waters) provides a better representation of water cluster anions, which do not behave like the bulk hydrated electron at this size.^{37–39} Most importantly, we see that fluctuations are critical for understanding the nature of the hydrated electron and having only a handful of explicitly treated waters is not sufficient to pin down the correct fluxional behavior.

METHODS

All of our *ab initio* dynamics calculations were performed using the Q-Chem software package.⁴⁰ The coordinates of Kumar et al.'s model, optimized using the B3LYP functional, were used for the initial geometry for both the 4- and 16-water systems.¹² We also used the IEFPCM⁴¹ (integral equation formalism polarizable continuum model) chosen by Kumar et al., with the constants chosen to represent the dielectric behavior of bulk liquid water. For calculating VDEs using PCM, we used nonequilibrium solvation calculations, which separate the fast and slow parts of the ionization process.⁴² We chose a relatively large triple- ζ basis set, 6-311++G(d,p), which we verified was sufficiently big for our relatively small systems; we note that other groups have used smaller basis sets in hydrated electron simulations and were able to obtain cavity-structure hydrated electrons,¹⁴ so the size of our chosen basis set is not structurally limiting. In the Supporting Information (SI), we

show that additional basis functions placed at the center of the cluster make virtually no difference to either the calculated spin density or vertical detachment energy. The nuclei, including the water protons, were treated classically, with the Born–Oppenheimer molecular dynamics (BOMD) propagated via the velocity Verlet algorithm with a time-step of 0.5 fs. The 4-water model was propagated in the microcanonical ensemble, and the 16-water model was propagated in the canonical ensemble using the Nose–Hoover chain thermostat to restrain the system to room temperature.⁴³ The average temperature of the 4-water system also was ~ 300 K, but with large fluctuations as expected for the small number of classical particles in the system, as shown in the SI. The VMD software package was used to visualize the molecular trajectories including the electron spin density.⁴⁴ Further calculational details, including those of the mixed quantum/classical models run for comparison purposes, are also given in the SI.

Our first set of trajectories were run using the standard hybrid B3LYP functional,⁴¹ as this was one of the main functionals used by Kumar et al. to analyze their 0 K structure of the 4-water hydrated electron. We ran three 10 ps B3LYP-based BOMD trajectories with four explicit waters plus PCM and an excess electron and found that all three trajectories were unbound: no matter what we chose for the initial condition, after a relatively short period of time, one of the four water molecules always moved away to a point where it no longer interacted with the excess electron. In other words, even though the 0 K minimum with the B3LYP functional has a well-defined tetrahedral cavity geometry with all four waters stabilizing the electron, the thermal energy available at roughly room temperature is enough to completely break the 4-water system apart, as described in more detail in the SI.

Given the difficulties in producing any physically meaningful geometries with the B3LYP functional, we turned next to a more sophisticated range-separated hybrid functional, the BNL functional;^{45,46} as far as we are aware, this is the first time an optimally tuned range-separated hybrid function has been used to simulate the hydrated electron. We successfully used the BNL functional, with the same triple- ζ basis set used here, in the past to predict the photoelectron spectra of water cluster anions with 4–6 water molecules, and we found that with the appropriate choice of the range separation parameter, we could reproduce water cluster anion VDEs calculated at the eom-IP-CCSD level of theory (with a quad- ζ basis plus diffuse functions) with better than 1% accuracy.³⁷ Thus, for the current work including four waters and PCM, we optimized the range-separation parameter to a value of 0.08 bohr^{-1} to satisfy Janak's theorem,⁴⁷ as described in the SI, and then ran a full set of BNL-based BOMD trajectories. We note that there is no empirically optimized dispersion correction available for the BNL functional. We found that, indeed, the BNL-based 4-water plus PCM and excess electron system remained intact with thermal fluctuations averaging around room temperature, so these trajectories form the basis for all of the results presented below. We also chose the BNL functional for our 16-water BOMD trajectories, reoptimizing the range separation parameter for this larger system to a value of 0.065 bohr^{-1} . For both systems, we chose uncorrelated configurations separated by at least 100 fs for our calculations of ensemble-averaged properties, which are discussed in the next section. We also ran mixed quantum/classical simulations of the hydrated electron using both the Turi–Borgis (TB)⁹ and Larsen–Glover–Schwartz (LGS)¹⁶ pseudopotentials for comparison to the

limits of cavity and noncavity models, respectively, as described in the SI.

RESULTS AND DISCUSSION

For all of the controversy over the structure of the hydrated electron, it has not been clear how one can calculate the full range of experimental properties from *ab initio* simulations that of necessity have limited numbers of water molecules and/or short trajectory times. Given the success of Kumar et al.'s model at 0 K,¹² we thought that extending the model to include dynamics would provide an interesting test of the role of fluctuations and entropy in the calculated properties of the hydrated electron, particularly as we have recently shown that entropic effects are important in determining the properties of mixed quantum/classical hydrated electron models.⁴⁸ As described in the previous section, however, the 4-water *ab initio* model whose properties were largely independent of the choice of functional at 0 K becomes highly dependent on the choice of functional when dynamics are included. In fact, as mentioned above, we found that the BOMD trajectories we ran were unstable to dissociation of a water molecule when using the B3LYP functional, but that the four waters and electron plus PCM held together when using the range-separated hybrid BNL functional. This provides the first indication that the minimalist *ab initio* model is not entirely robust, and as we show below, the results emphasize the importance of including fluctuations as critical to understanding any calculated properties of the hydrated electron.

Structure of Minimalist Room-Temperature BOMD Models of the Hydrated Electron. We start by examining the results of our BNL-based 4-water-plus-PCM BOMD trajectories of the hydrated electron. The most significant thing we observe is a large change in average structure from the 0 K geometry. The 0 K tetrahedral structure, which we optimized including a constraint to hold the tetrahedral geometry (see the SI for details on what happens when this constraint is relaxed), is shown in Figure 1a. As discussed by Kumar et al.,¹² the 0 K excess electron largely occupies a cavity between the molecules; the distances between the electron and other atoms correspond to the δ functions in the pair distribution function shown in Figure 2d. In contrast, the average structure of the room-temperature 4-water BOMD model has the four water molecules tending to reside inside the bulk of the electron's charge density, as seen in the red and blue curves in Figure 2a. As a comparison to the extremes in possible hydrated electron structures, we also show in Figure 2b,c, respectively, the pair distribution functions of the closest four water molecules for the Turi–Borgis (TB) cavity⁹ and Larsen–Glover–Schwartz (LGS) noncavity¹⁶ mixed quantum/classical hydrated electron models. Clearly, when fluctuations are included, the 0 K *ab initio* cavity-like model becomes much more reminiscent of the LGS noncavity model than the more traditional TB cavity model.

To test the effect of system size, we also carried out a similar analysis for the version of the model with 16 explicit waters. Starting from the optimized structure by Kumar et al. with a tetrahedral cavity around the excess electron, shown in Figures 1c and 2h, we find that the average structure of the room-temperature model collapses in much the same way as with the 4-water version, as seen in Figures 1d and 2e. For comparison, we also calculated the radial distribution functions of both the TB and LGS models using only the 16 closest water molecules, shown in Figure 2f,h. Clearly, like the 4-water model, the radial

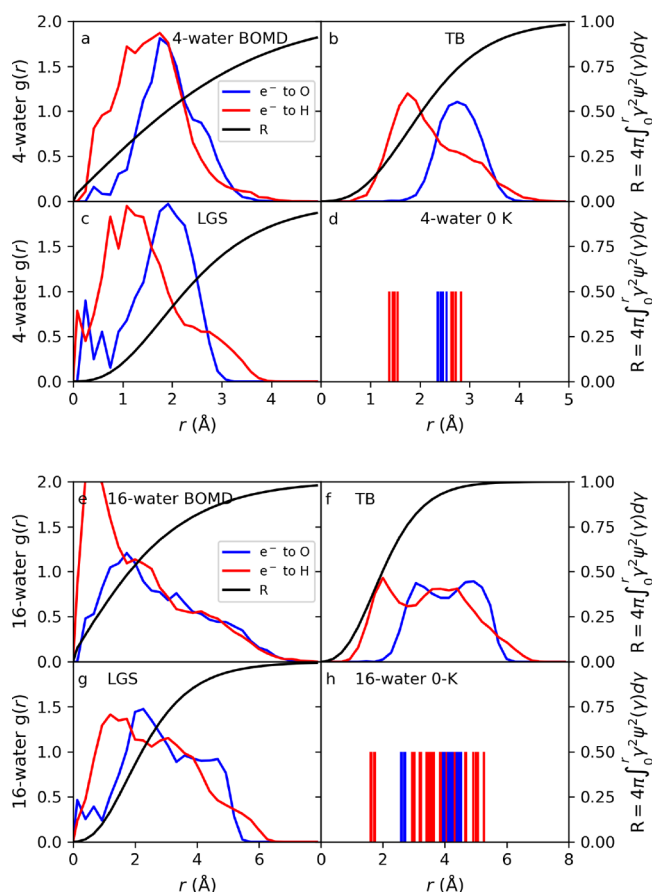


Figure 2. Radial distribution functions (RDFs) from the excess electron's center-of-mass for water hydrogen (red curves) and oxygen atoms (blue curves) for (a, e) the BNL-BOMD (this work), (b, f) the TB,⁹ and (c, g) the LGS¹⁶ hydrated electron models. The red and blue vertical lines coming up from the abscissa in panels d and h represent the distance between the electron's center-of-mass and the hydrogen and oxygen atoms for the waters in the 0 K tetrahedral model whose structure is shown in Figure 1a,c. The top and bottom rows of plots correspond to the 4- and 16-water room-temperature BOMD models, respectively. All of the RDFs were normalized by using the number density of bulk water and calculating the volume of 4- or 16-water molecules. The results show clearly that the room-temperature BNL-BOMD models' excess electron more closely resembles the noncavity LGS model than the TB cavity model and bears little resemblance to the 0 K structure. The black curves in each panel show $R = 4\pi \int_0^r \gamma^2 \psi^2(\gamma) d\gamma$ where $\psi(\gamma)$ is the wave function/spin density of the excess electron for each model.

distribution function of the 16-water room-temperature BOMD is much more similar to the LGS noncavity model than to the traditional cavity model. This suggests that *ab initio* BOMD models of the hydrated electron with minimalist numbers of waters plus PCM suffer from all the same problems as the LGS model, which is not well-accepted in the literature.^{4,16,22}

Figure 1b shows a representative snapshot from the 4-water room-temperature BOMD trajectories, respectively. Unlike the 0 K structure, which had the water molecule H atoms pointing toward the electron's center-of-mass (i.e., H-bond solvation of the electron), the dynamical structure suggests that, with thermal energy, the water molecules prefer to make H-bonds with each other rather than with the excess electron. The preference is strong enough that the four waters on average

adopt a flat, ring-like geometry reminiscent of the gas-phase water tetramer^{49,50} rather than an arrangement that looks like the 0 K tetrahedral cavity structure. This preference to maintain the water–water H-bonds is also consistent with what is known from studies of noncavity models, which suggest there is a temperature-dependent free energy penalty for creating empty volume and breaking the pure water H-bonding network.^{4,16,48}

The 16-water snapshot seen in Figure 1d, on the other hand, bears a striking resemblance to what we saw in previous simulations of water anion clusters (using the same DFT functional) with similar numbers of water molecules but without the use of PCM.³⁷ The electron clearly prefers to sit on the surface of the cluster, stabilized by H-bonds of the few waters in the cluster that are adjacent to it. The other waters in the cluster make H-bonds with each other, and the addition of PCM seems to make little difference to the overall outcome, as we verified with a set of calculations using the same uncorrelated configurations, but without the use of PCM. We explore what happens without PCM in detail in the SI, but the general result is that the average distance between the center of mass of the electron and the center of mass of the cluster is largely unaffected by the presence of PCM. The cluster ionization energy does shift in the presence of PCM, as expected, but as discussed below, the amount of this shift is not nearly enough to recover the experimental ionization energy of the bulk hydrated electron. Thus, PCM simply shifts the electron binding energy but does not alter the structure to mimic a bulk system instead of that of a small cluster anion. This shows explicitly that PCM cannot be used as a substitute for explicit water molecules when simulating the properties of the bulk hydrated electron. Since it is well-known that water anion clusters in the size range of a few tens of water molecules do not have the properties of the bulk hydrated electron,^{38,39} this result strongly suggests that *ab initio* simulations that also use only a few tens of water molecules are missing important physics underlying this object. We believe that hundreds of waters are necessary for a correct description of this object, something that is unfortunately currently out-of-range in terms of computational cost for BOMD simulations.

As a way to help quantify the arrangement of the water molecular orientation relative to the electron's center-of-mass, we calculated the asphericity A of the four closest water molecules in each simulation to the electron, defined from the positions of the water O atoms as

$$\langle A \rangle = \frac{\langle (\text{Tr}^2 - 3M) \rangle}{\langle \text{Tr}^2 \rangle} \quad (1)$$

where $\text{Tr} = R_1^2 + R_2^2 + R_3^2$ and $R_1, R_2,$ and R_3 are the eigenvalues of the gyration tensor, and $M = R_1^2 R_2^2 + R_1^2 R_3^2 + R_2^2 R_3^2$.⁵¹ With this definition, A is zero for a three-dimensionally symmetric arrangement of the water molecules, 0.25 for a two-dimensionally symmetric arrangement, and 1.0 for a linear one-dimensional arrangement. Indeed, for the 4-water 0 K structure of Kumar et al., we calculate $A = 0.008$, a value near zero as expected. For the room-temperature BOMD trajectories, A never approaches zero but instead fluctuates around an average value of 0.34 for the 4-water model (Figure 3a) and 0.48 for the 16-water model (Figure 3b), suggesting an average local geometry of the waters near the electron that is closer to flat, consistent with the snapshots shown in Figure 1b,d.

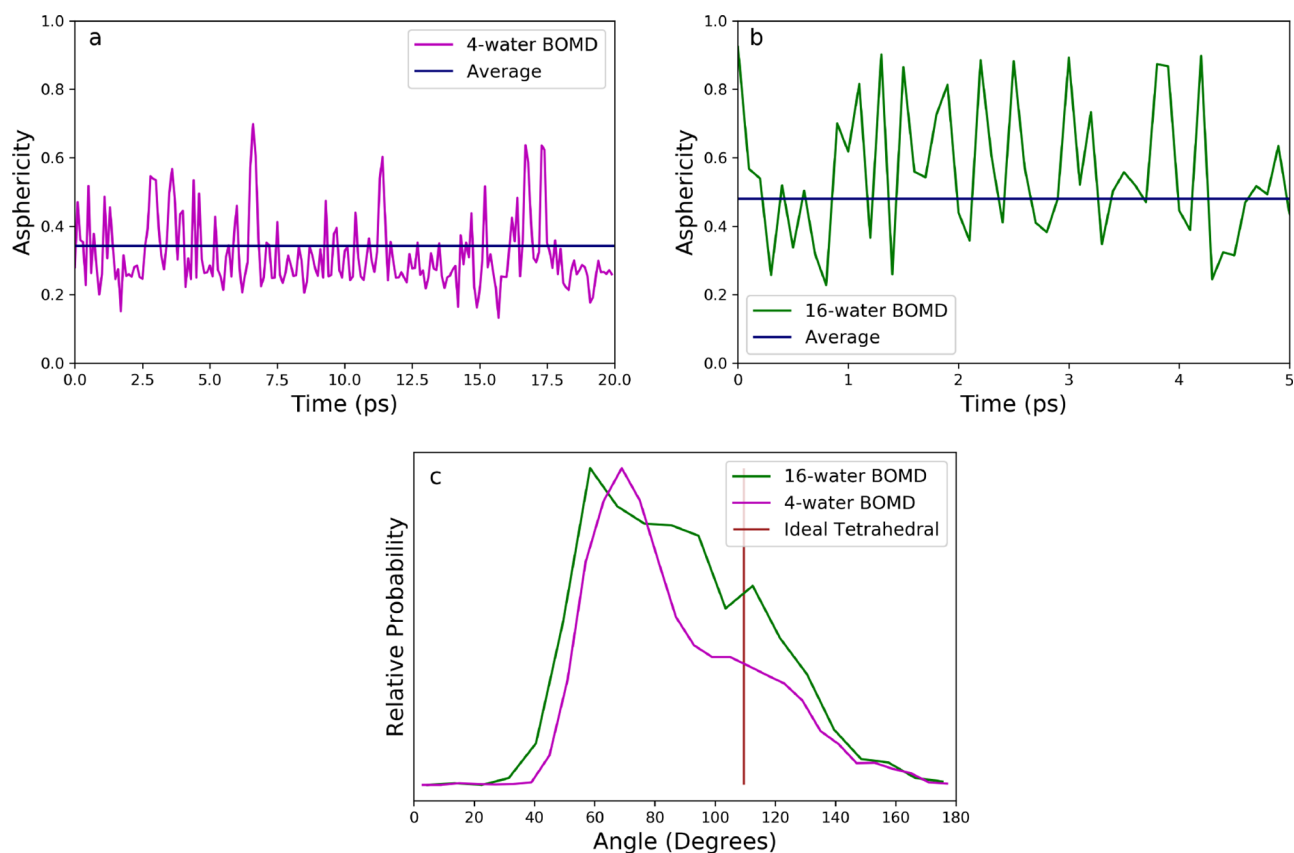


Figure 3. (a, b) Asphericity A (eq 1 in the text) of the room-temperature 4-water and 16-water BOMD model of the hydrated electron, with values calculated from uncorrelated configurations every 100 fs. The navy horizontal line shows the average asphericity value of 0.34 for the 4-water model calculated from five 20 ps long trajectories and 0.48 for the 16-water model calculated from four 5 ps long trajectories. Clearly, thermal fluctuations destroy any tetrahedral memory of the 0 K structure, as the asphericity value never approaches zero. (c) Distribution of angles between vectors connecting the electron's center-of-mass to the water O atoms for the same uncorrelated configurations in parts a and b. If the O atoms are arranged perfectly tetrahedrally from the electron's center-of-mass, as in the 0 K structure, the distribution is a δ function at 109.5° . The fact that the room-temperature average is far from this value reflects the more planar average structure seen in Figure 1b,d.

Figure 3c shows the distribution of angles between the vectors connecting the electron's center-of-mass to the four closest water O atoms for the 4- and 16-water BOMD models, respectively, which for the 0 K tetrahedral arrangement both had a value very close to 109.5° . When thermal fluctuations are included, the average angle is closer to 70° for both BOMD models, another signature of the fact that the water molecules prefer to make H-bonds with themselves rather than with the excess electron at room temperature. Overall, Figure 3 indicates clearly that when fluctuations are accounted for, the local molecular geometry is not even approximately tetrahedral, so that the 0 K structure is not a good indicator of the average structure at room temperature.

One subject of current interest in the literature is how much the hydrated electron's wave function overlaps with the closest surrounding water molecules. In previous work, we calculated the "direct overlap" Θ of the hydrated electron for different simulation models, defined as the fraction of the excess electron that resides within a certain distance r_c of the O atom on each of the surrounding water molecules:⁴

$$\Theta = \left\langle \sum_{i=1}^{n_{\text{moles}}} 4\pi \int_0^{r_c} r_i^2 |\Psi(r_i)|^2 dr_i \right\rangle \quad (2)$$

Here, r_c was chosen to be 1.0 \AA , the same as the water O–H bond length and thus a good measure of the size of water's

core molecular orbitals. The results for the room-temperature BOMD models as well as for the four instantaneously closest waters in the TB and LGS models are given in Table 1 as the "4-water direct overlap". Not surprisingly, the TB cavity model shows a small direct overlap, indicating that the electron is strongly repelled from the water molecular cores, with little fluctuation in overlap as expected for such a strongly repulsive model.⁴⁸ In contrast, the 4-water BOMD results have an average value and standard deviation that are quite similar to that of the noncavity LGS model, suggesting that when thermal fluctuations are included, the electron becomes more likely to overlap the nearby waters. It is worth noting that the BNL-based cavity structure at 0 K also has a high direct overlap with the explicit waters. This likely reflects the fact that the water molecules at 0 K strongly interact with the excess electron due to a lack of hydrogen bonding with each other (or any exterior water molecules) and indicates that the nature of the 0 K *ab initio* hydrated electron model is fundamentally different than the TB model, even though both have central cavities.

Table 1 also shows that the 16-water BOMD simulation has a smaller direct overlap when both the closest 4 and all 16 water molecules are considered. For comparison, we also calculated the direct overlap with the 16 closest water molecules in the TB and LGS models, which shows that, for the 16-water BOMD model, the direct overlap value is more similar to that of the TB cavity model. This is a direct

Table 1. Direct Overlap Θ ,^a Cavity Order Parameter q^{cav} , and Radius of Gyration of the Experimental Hydrated Electron and the TB, LGS, and Room-Temperature BNL-BOMD Models^b

	4-water direct overlap	16-water direct overlap	cavity order param	radius of gyration (Å)
expt	N/A	N/A	N/A	2.45
4- BOMD	8.65% ± 1.44%	N/A	0.766 ± 0.38	2.92
16- BOMD	3.15% ± 1.41%	4.25% ± 1.44%	0.768 ± 0.50	3.21
TB	2.98% ± 0.81%	4.57% ± 0.91%	0.012 ± 0.06	2.42
LGS	8.64% ± 2.77%	14.1% ± 2.85%	0.886 ± 0.43	2.5

^aEquation 2 with n_{molcs} running over either the 4 or 16 closest water molecules. ^bThe values after the \pm signs are the standard deviation for the fluctuating direct overlap and cavity order parameters. The results show that the as far as overlap is concerned, the 4-water BOMD model resembles the LGS non-cavity model more than the TB cavity model and vice versa for the 16-water BOMD model. The fact that the 0 K *ab initio* tetrahedral structure has such a high direct overlap of 14.3% shows that the 0 K Kumar et al. model still behaves fundamentally differently than the traditional TB cavity model.

reflection of the fact that, in the 16-water model, the electron density is more water-anion-cluster-like, with the bulk of the electron density protruding into the PCM outside the water molecules, as seen in Figure 1d. We believe that this behavior is unrepresentative of the bulk hydrated electron, as EPR experiments suggest that there should be reasonable overlap of the hydrated electron with the nearby waters.^{17,18} Thus, for minimalist simulations in this size range, adding more waters to the BOMD simulation does not necessarily improve things as far as representing the bulk object is concerned.

Finally, we also characterized the cavity/noncavity nature of different hydrated electron models using a cavity order parameter that we recently introduced in another context.⁴⁸ The order parameter q^{cav} is defined as

$$q^{\text{cav}}(R^N) = \sum_{i=1}^N S(|R^i - r_e|) \quad (3)$$

$$S(r) = \frac{1}{\exp[\kappa(r - r_e)] + 1} \quad (4)$$

where R^i is the distance of the i th water molecule's O atom from the electron's center-of-mass. This function essentially integrates the number of water molecules within the distance of r_e of the electron's center. If we take the four instantaneously closest waters in the TB and LGS models as limits of cavity and noncavity behavior, respectively, then the choice of $r_e = 1.75$ Å and $\kappa = 10$ Å⁻¹ gives a value of q^{cav} of 0.89 for LGS and essentially zero for TB. This means that q^{cav} provides a nice distinction between different possible hydrated electron structures, as summarized in Table 1. The results show that the minimalist BOMD models have a similar q^{cav} as the LGS model, demonstrating that thermal energy is able to drive water molecules into the interior of what was otherwise a stable 0 K cavity structure. The fact that the 16-water BOMD model has a similar value of q^{cav} but a different value of Θ as the 4-water model serves to emphasize that the presence of interior waters does not necessarily imply significant overlap and vice versa. The large standard deviation in q^{cav} for both the LGS

and BOMD models indicates that the number of waters residing close to the electron's center is highly fluxional, so that entropy places a large role in the cavity or noncavity structure of the excess electron. The TB model shows essentially no fluctuations of water into the cavity interior, and we have argued in previous work that it is these fluctuations that are responsible for the temperature dependence of the hydrated electron's absorption spectrum and excited-state lifetime.^{25,48}

Overall, when thermal energy is added to the minimalist *ab initio* model of Kumar et al., entropic contributions modify the overall structure from cavity-like to more non-cavity-like. Going from 4 to 16 water molecules makes little difference other than producing a smaller direct overlap value, which may actually increase the disagreement with experiment. In fact, in the presence of thermal fluctuations, the dynamical version of Kumar et al.'s model behaves quite a bit like the mixed quantum/classical LGS model and thus likely suffers from the same shortcomings, such as giving the wrong sign of the molar solvation volume based on the average number of interior waters.^{21,22} We note that most previous *ab initio* simulations of the hydrated electron, most of which used more water molecules than we use here, only minimally characterize the structure produced in their simulations: they usually plot only the radial distribution function,^{11,13,15} or in some cases present only a few snapshots¹⁴ to conclude that the excess electron resides in a cavity. With the various structural parameters employed in this section, A , Θ , q^{cav} , etc., it is possible to numerically compare the structures of different hydrated electron models, and we hope that parameters like these can be used by other groups in the future. To understand the importance of a hydrated electron model's structural details, we turn in the next section to testing the BOMD models against multiple different experiments. However, the most important conclusion is that, for any hydrated electron model, a 0 K or average structure is inadequate to explain the properties of the hydrated electron: Clearly, thermal fluctuations are an extremely important part of the behavior of this statistically fluctuating quantum object.

Experimental Predictions of Minimalist BOMD Models. One of the successes of the 0 K version of Kumar et al.'s minimalistic *ab initio* model of the hydrated electron is that when the distances of the four water molecules were adjusted to match the experimental VDE, which was reported to be around 3.3–3.7 eV,^{32–35} the resulting cavity size and absorption spectrum were in good agreement with experiment.¹² This leads to the question of how well that agreement persists when thermal fluctuations are added to the model and the presence of the central cavity is effectively destroyed.

We begin by examining the VDE of the minimalist BOMD hydrated electron models by calculating what would be expected in a photoelectron spectroscopy experiment. Since we optimally tuned the range-separation parameter of the BNL functional used in the simulations, as described in the SI, the singly occupied molecular orbital (SOMO) energy is by construction equal to the ionization energy for each simulated configuration. Thus, we simply binned up the SOMO energies of uncorrelated configurations to simulate the steady-state photoelectron spectrum, the results of which are shown in Figure 4. The figure shows that when thermal energy is added to the system, there is a large shift of the VDE toward lower binding energies relative to the 3.2 eV value of the 0 K 4-water plus PCM structure. Clearly, thermal motions drive a lot of repulsive overlap between the excess electron and the nearby

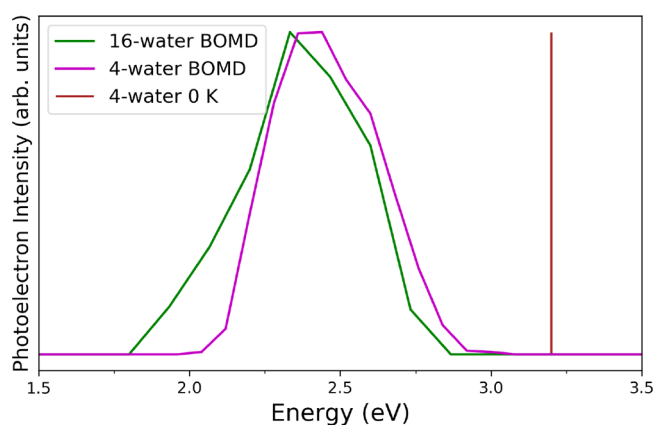


Figure 4. Photoelectron spectra simulated by binning the SOMO energies from uncorrelated configurations drawn from the room-temperature BOMD trajectories of the 4-water plus PCM BOMD model (magenta curve), and the 16-water plus PCM BOMD model (green curve). Compared to the experimental VDE value of 3.4–3.7 eV and the 4-water 0 K calculated VDE of 3.2 eV, represented as a brown vertical line, it is clear that thermal motions significantly reduce the binding of the excess electron for both *ab initio* dynamic models.

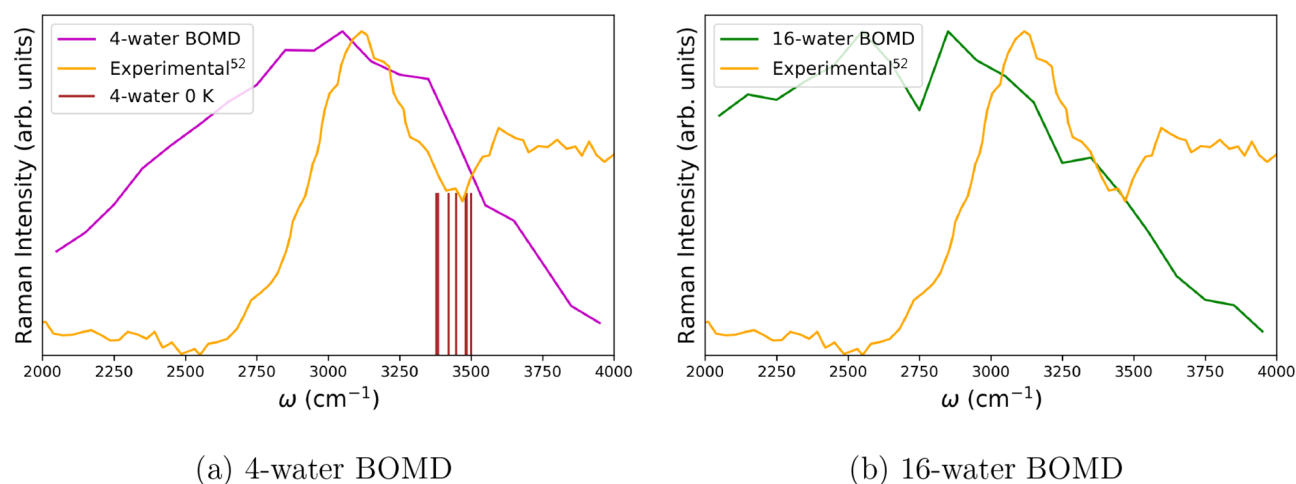
water molecules, making it easier to detach the electron, leading to a predicted VDE that is in contrast with experiment. Surprisingly, increasing the number of BOMD waters from 4 to 16 makes little difference in the predicted VDE, which is another sign that these minimalist models do not adequately represent the nature of the experimental bulk hydrated electron.

Next, we turn to the hydrated electron's resonance Raman spectrum. Experimentally, the hydrated electron's resonance Raman spectrum looks much like that of bulk water's, but with a red-shifted and broadened O–H stretch.⁵² In previous work,³⁰ we estimated the resonance Raman spectrum of mixed quantum/classical models of the hydrated electron using a frequency/electric field map parametrized to reproduce the Raman spectrum of bulk water^{53–55} and found that the LGS

noncavity model provided excellent agreement with experiment whereas the TB cavity model showed a qualitatively incorrect (blue-shifted and narrowed) O–H stretch.³⁰ A set of recent QM/MM calculations, however, has shown that cavity model hydrated electrons can qualitatively reproduce the Raman spectrum of the hydrated electron, presumably due to a small amount of occupation of the water LUMO by the excess electron that cannot be accounted for in mixed quantum/classical simulations.²³ These calculations also showed that a cavity hydrated electron structure could also provide an explanation for the isotopic splitting of the water bend that is missed by the LGS model.²³

To calculate the resonance Raman spectrum of any object, the various vibrational normal modes need to be weighted by how much they are displaced upon electronic excitation. We have shown previously, however, that the average displacement of the O–H stretch upon excitation of the electron is roughly constant for water molecules that are within 4 Å of the electron's center and fairly negligible for waters outside this distance.³⁰ If we take advantage of this fact, we can estimate the resonance Raman spectrum for the room-temperature BOMD simulations by calculating the *ab initio* frequencies of the waters in this range and simply binning them with equal weight, as shown in Figure 5. For the water molecules outside of the 4 Å range, instead of simply excluding them from the Hessian matrix calculation, we employed a vibrational subsystem analysis⁵⁶ in which vibronic interactions between the included and excluded molecules are implicitly folded into the calculation. We note that the Q-chem software we used for these simulations does not support Hessian matrix calculations with the IEFPCM model, so for calculation of the normal modes for our selected uncorrelated configurations, we used CPCM (conductor-like PCM) instead.⁵⁷

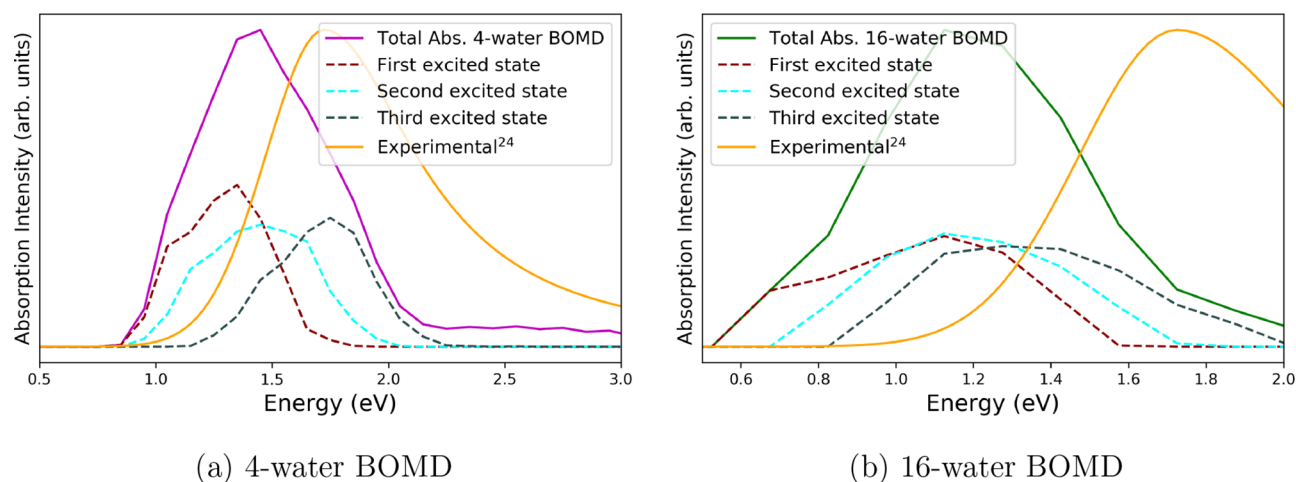
Figure 5a shows that both the 4-water BOMD and experimental⁵² resonance Raman spectra have a similar peak O–H stretch peak location near 3100 cm⁻¹, an agreement which is better than most other models in the literature.^{23,30} The 16-water BOMD resonance Raman spectrum in Figure 5b shows a peak that is further red-shifted, so that the addition of



(a) 4-water BOMD

(b) 16-water BOMD

Figure 5. Resonance Raman spectra calculated from (a) the 4-water (magenta curve) and (b) 16-water (green curve) room-temperature BOMD simulation (see text for details) and measured by experiment (yellow curves in both panels).⁵² The high fluctuations of both the geometry and electron density in the BOMD trajectories cause the calculated resonance Raman spectrum to be much broader than the experimental spectrum. For comparison, the red δ functions in panel a represent the normal modes of the 4-water 0 K tetrahedral structure, which are significantly blue-shifted compared to experiment, suggesting that the 0 K 4-water model does not adequately reproduce this feature of the experimental hydrated electron.



(a) 4-water BOMD

(b) 16-water BOMD

Figure 6. Room-temperature BOMD model predicted absorption spectra, calculated via TD-DFT using the BNL functional on uncorrelated snapshots along the ground-state trajectory for (a) the 4-water + PCM minimalist BOMD model (magenta curve), and (b) the 16-water + PCM minimalist BOMD model (green curve), respectively. Transition dipoles to the lowest 10 excited states were used to build the calculated absorption spectrum. The dashed red, cyan, and gray curves represent the contributions of transitions to the first, second, and third excited states to the total absorption spectrum, respectively. The orange curve in each panel shows the experimental absorption spectrum. The BOMD absorption spectra are red-shifted relative to experiment in both models due to a too-large radius of gyration caused by inadequate electron confinement of the PCM.

the 12 explicit water molecules actually makes the agreement with experiment worse. However, we also see that both the 4-water and 16-water BOMD calculated spectra are far too broad compared to experiment. We believe that this is a reflection of the fact the large fluctuations of the hydrated electron's structure in these models are also causing large fluctuations of the calculated normal-mode frequencies. Thus, like the LGS model,⁴⁸ the broad width of the calculated resonance Raman spectra demonstrates that the room-temperature BOMD model overly fluctuates compared to the experimental hydrated electron. In contrast, the 4-water 0 K cavity structure has a predicted *ab initio* Raman spectrum that is too blue-shifted compared to experiment,¹² suggesting that neither the H-bonding environment of the waters nor the overlap of the electron's wave function with the water is captured correctly at 0 K.

As mentioned in the **Introduction**, one of the most standard experimental benchmarks of hydrated electron models is the optical absorption spectrum. The absorption spectrum is directly related to the radius of gyration of the electron's ground-state wave function, as explicitly connected through spectral moment analysis.²⁰ Since DFT-based simulations do not provide reliable excited states for calculating the transition dipole matrix elements underlying the optical absorption, we calculated the lowest 10 excited states using time-dependent DFT (TD-DFT) using the same optimally tuned BNL functional on a series of uncorrelated configurations from each of the BOMD ground-state trajectories. The transition dipoles between the ground and excited states were then computed and binned according to their energy gaps, producing the calculated spectrum shown in **Figure 6**. The general shape and width of both the 4-water (panel a) and 16-water (panel b) room-temperature BOMD spectra are similar to the experimental spectrum,²⁴ but the positions are significantly red-shifted, reflecting the fact that the average radius of gyration of the room-temperature BOMD electrons is too large, as discussed further below. As is typical with nearly every hydrated electron model, the calculated spectra are

dominated by transitions to the first three excited states, so-called s-to-p-like transitions.

To verify the reasons for the red-shift of the room-temperature-BOMD-simulated *ab initio* hydrated electron absorption spectra, we calculated the excess electron's radius of gyration using the spin density, as summarized in **Table 1**. The results indicate that, unlike the more standard TB and LGS mixed quantum/classical models, whose predicted absorption spectra agree generally well with experiment,^{9,16} the radius of gyration of the BOMD models is indeed larger than the experimental value. This is because the polarizable continuum model is simply unable to confine the excess electron as much as Pauli exclusion from explicit water molecules, allowing the BOMD electron to balloon into the region where there are no explicit waters present. This idea not only explains the red-shift of the calculated absorption spectra, but also the decreased VDE, as it is well-known that the VDE varies inversely with the hydrated electron's radius of gyration.^{11,19}

We note that other *ab initio* simulations also produce a radius of gyration that is somewhat too large,^{11,14} suggesting that it is quite difficult for DFT-based BOMD to correctly capture the true spatial extent of the hydrated electron. This is because it is challenging to accurately account for the small amount of mixing of the electron's wave function into the surrounding water LUMOs, which has a large effect on the radius of gyration because these waters have molecular orbitals whose charge density resides far from the electron's center-of-mass, and because it is difficult to properly capture thermal fluctuations with unrealistically small systems and limited sampling. Overall, we believe that the rough agreement of the 0 K minimalist model with experimental values such as the radius of gyration, VDE, vibrational spectrum, and ESR coupling is largely a coincidence, as the dynamically fluctuating versions of this model show very different behavior than the single, unrepresentative 0 K snapshot.

CONCLUSIONS

In this paper, we have extended Kumar et al.'s 0 K minimalist water-plus-PCM *ab initio* model of the hydrated electron¹² to include thermal fluctuations at room temperature via BOMD. We find that, even though the 0 K model is in good general agreement with experiment for the VDE and radius of gyration (but not the resonance Raman spectrum), when thermal motions are included, this simple model is inadequate to correctly capture the physics of the hydrated electron. Unlike at 0 K, the BOMD models become highly dependent on the choice of DFT functional employed, with the common B3LYP hybrid functional actually leading to detachment of one of the four waters. With the optimally tuned BNL range-separated hybrid functional, which did an excellent job reproducing the properties of small water anion clusters,³⁷ we find that the minimalist BOMD hydrated electron model behaves more like the noncavity LGS model than any traditional cavity model in terms of its structure. The details of the BOMD model, such as the amount of electronic overlap of the excess electron with the surrounding water, do depend on how many waters are treated explicitly, but the general trend is that no central cavity is observed. This means that minimal BOMD models have all the same flaws as the LGS noncavity model, including giving the wrong sign of the molar solvation volume,^{21,22} in addition to a too-large radius of gyration that leads to a red-shifted absorption spectrum and lower VDE than experiment.

It is worth noting that previous DFT-based hydrated electron simulations using 32 QM water molecules showed a cavity-like structure,¹¹ while the 16-water simulations performed here show no sign of cavity behavior. This might suggest that the transition to cavity-like behavior happens between 16 and 32 water molecules, but this seems unlikely given that there is no sign of this transition in experiments on water cluster anions.^{39,58} Instead, we believe that the use of MM waters and/or the use of periodic boundary conditions approximate bulk behavior very differently than the PCM model used in Kumar et al.'s model and our extension of it here. We are not aware of any systematic exploration of finite-size effects in hydrated electron simulations using periodic boundary conditions, but the simulations presented here show that even 16 waters are nowhere near enough to capture the correct bulk behavior, even with the addition of PCM.

Given that the minimalist model works reasonably well at 0 K, why does it fail at room temperature? In the 0 K version of the minimalist model, Kumar et al. found that adding up to a dozen more water molecules made little difference to the calculated excess electron's properties. However, when thermal motion is added to the model, it becomes clear that the PCM is unable to provide adequate confinement of the excess electron, even when up to 16 explicitly treated waters are used. The use of PCM merely shifts the electron binding energy, although not enough to be in agreement with experiment, and is not capable of altering the structure of the excess electron relative to what would have been observed in a small water cluster anion. Even if we were to use additional explicitly treated waters in a BOMD model, however, it still remains unclear that DFT, even with an optimally tuned range-separated hybrid functional, provides a sound basis for the quantum chemistry of the bulk object. Non-DFT-based *ab initio* simulations of the hydrated electron have been performed,¹⁴ but the computational expense even with a limited number of water molecules (to date less than 50)

precludes sufficient statistics to make meaningful comparisons with experiment. Our results indicate that, whatever model is used to simulate the hydrated electron, replacing water molecules outside of the first two solvation shells with the PCM is not adequate for correctly capturing the physical behavior of this object.

The most important conclusion of this work, however, is the importance of fluctuations in determining the properties of the hydrated electron. The dramatic structural and electronic changes we observed between the 0 K and room-temperature versions of the 4- and 16-water models show that thermal motions are critical to any proper description of the hydrated electron. Even for cavity models, treating the electron as a quasi-halide ion does not make sense, as the size, shape, and amount of overlap of the electron with the nearby waters are constantly fluctuating due to thermal motions.⁴⁸ Most of the *ab initio* simulations in the literature have not addressed the effects of fluctuations,^{11,13,14} many of which can be simply captured with parameters such as the direct overlap Θ or q^{cav} coordinate, described above. Entropy is clearly the key to the temperature-dependent properties of hydrated electrons that are not well-described by cavity models,^{25,26,29,48} so that any model of the hydrated electron, no matter how minimalist, must include temperature-driven fluctuations in order to provide a faithful picture of this fascinating object.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpbc.0c06356>.

Details of the optimization of the BNL range separation parameter, B3LYP trajectories not discussed in the main text, and other dynamical structural parameters (PDF)

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Notes

The authors declare no competing financial interest.

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