

# **Structure, dynamics, and reactivity of hydrated electrons by *ab initio* molecular dynamics**

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## Conspectus

Properties of electrons solvated in water are investigated by means of *ab initio* molecular dynamics simulations. This approach, applied to a model system of a negatively charged 32 water cluster, allows us to characterize structural, dynamical, and reactive aspects of the hydrated electron using an all (valence) electron description. We show that at ambient conditions the electron solvates into a cavity close to the surface of the liquid cluster. Such a cavity is more flexible and penetrable to water molecules than that around negatively charged ions due to the lack of the stabilizing positively charged nucleus in the solvated electron case. The dynamical process of electron attachment to a neutral water cluster is strongly temperature dependent. At ambient conditions the electron relaxes in the liquid cluster and becomes indistinguishable from an equilibrated solvated electron on a picosecond timescale. In contrast, for solid, cryogenic systems the electron only partially localizes at the outside of the cluster, being trapped in a metastable, weakly bound “cushion-like” state. Strongly bound states at cryogenic conditions could only be prepared by cooling equilibrated liquid negatively charged clusters. This demonstrates how different isomers of electrons in cryogenic clusters can be observed experimentally. At the same time, the present results question the applicability of direct extrapolations of properties of cryogenic negatively charged water clusters to those of electrons in the liquid bulk. *Ab initio* molecular dynamics represents a unique computational tool for investigating the reactivity of the solvated electron in water. As a prototype, the electron-proton reaction is followed in the 32 water cluster. We provide the molecular mechanism of this seemingly

elementary reaction showing in accord with experiment that it is a proton transfer process which is not diffusion limited but controlled by a proton-induced deformation of the solvent shell of the excess electron. Using these examples we demonstrate the necessary ingredients of a successful density functional methodology for the description of the hydrated electron, which has to avoid potential pitfalls, such as the self-interaction error, insufficient basis set, and lack of dispersion interactions. We also provide benchmarking of the employed density functional theory methods and outline the path to faithful *ab initio* simulations of dynamics and reactivity of electrons solvated in extended aqueous systems.

## 1. Introduction

The blue color associated with dissolution of alkali metals in ammonia has been observed already in the 19<sup>th</sup> century, but it was not until 1918 that the phenomenon became connected with solvated electrons.(1) It is common knowledge that this process is much more vigorous in water.(2) Therefore, it turned out not to be a practical way to investigate hydrated electrons, which were first prepared by pulse radiolysis of water only in 1962.(3) Since then, electrons in water were shown to act as key species in many radiation chemistry processes.(4) Their structure, dynamics, and reactivity have been, therefore, intensely studied by time resolved spectroscopies.(4-7) In short, these studies showed that initially non-equilibrium electrons, prepared by photoexcitation of solvated electrons or UV ionization of water or host species such as halide anions, relax fast but in a complicated fashion (depending on their preparation) to a localized, cavity-like structure of a mean radius of 2.5 Å. At the same time, the electron in water can, as a chemically unstable species, geminately recombine with OH or H<sub>3</sub>O<sup>+</sup> (or the halogen atom), or react with a whole plethora of scavengers like N<sub>2</sub>O or SF<sub>6</sub>. Recently, the cavity model of the solvated electron and its ability to interpret optical and EPR spectra(8) has been questioned and an alternative, diffuse electron model has been suggested(9) and immediately criticized.(10, 11) In the course of this paper, we come back to this issue in more detail.

Another experimental approach to hydrated electrons is based on investigating negatively charged water clusters of increasing size by photoelectron and IR spectroscopies.(12-15) Already a water dimer is capable of binding an excess electron,(12)

however, its character is very different from the bulk hydrated species. In small systems, these are weakly bound and very diffuse dipole-bound electrons, which reside at the exterior of the water cluster.<sup>(16)</sup> Upon increasing the cluster size, the binding energy of the excess electron increases and it is often assumed that it eventually approaches the aqueous bulk limit.<sup>(14, 17)</sup> However, this issue can be rather subtle since water clusters prepared by supersonic jet expansion are not liquid but rather amorphous solids. As data on electron binding in liquid water have recently become directly accessible experimentally,<sup>(17-20)</sup> applicability of cluster to bulk extrapolations has been vividly discussed recently<sup>(14, 15, 17, 21, 22)</sup> and will be also one of the subjects of this paper.

Experiments on hydrated electrons are paralleled by molecular calculations. On the side of large system sizes, electrons in big clusters and extended aqueous systems have been described using a pseudopotential.<sup>(9, 23-30)</sup> Within this approach, only the excess electron is treated as a quantum mechanical entity, while the rest of the system is described classically. The advantage is that the computationally most costly quantum mechanical part does not increase with system size, therefore, large systems ranging from clusters with several hundreds of water molecules to “infinite” (via periodic boundary conditions) aqueous bulk or slab systems can be addressed. The problematic part is the purely effective account for the electronic structure of water molecules excluding thus exchange interactions between all the electrons in the system, which may account for about 10-20% of the excess electron binding.<sup>(8, 31)</sup> Moreover, the results can only be as good as the underlying pseudopotential and can sensitively depend on its form and parameters.<sup>(10, 11)</sup> Finally, description of the chemical reactivity of the excess electron is in principle out of

reach of these pseudopotential methods.

For the above reasons it makes good sense to try to describe the electronic structure of the whole electron-water system quantum mechanically. Small anionic water clusters with up to about ten water molecules can be treated using accurate *ab initio* quantum chemical methods.<sup>(32, 33)</sup> Methods like coupled clusters with very diffuse basis sets, which account satisfactorily for electron correlation effects (in particular dispersion), are required for a quantitative description of the diffuse electrons weakly bound to small water clusters.<sup>(33)</sup> Upon increasing the cluster size the character of the excess electron gradually changes from such an external dipole-bound electron to a more strongly bound and compact species which starts to resemble the electron solvated in extended aqueous systems. Due to increase in binding and decrease in size of the electron, its description becomes easier as system size increases. This is fortunate, since one can hope that density functional theory (DFT) methods, applicable to large systems, could take over when coupled clusters and similar approaches are no more practical.<sup>(21, 22, 34-38)</sup> One has to, however, keep in mind the possible pitfalls of DFT like problems with dispersion interactions and the self-interaction error (SIE), the latter being particularly relevant for open-shell systems such as the solvated electron.<sup>(37, 39)</sup> Nevertheless, as we show in this article, when the potentially problematic issues with DFT are properly addressed, one can obtain a practical and faithful method for the description of the structure, dynamics, and reactivity of electrons solvated in large aqueous systems.

## 2. DFT simulations and analysis of the hydrated electron

The workhorse for our studies of the hydrated electron has been a negatively charged cluster comprising 32 water molecules.(21, 22, 36, 37) There is nothing particular about this number, the important thing is that such a cluster is already large enough to host a species that semi-quantitatively resembles an electron solvated in the aqueous bulk. While the size of the cluster is still far from allowing a fully quantitative modeling of extended systems, the cluster is big enough to possess both surface and interior regions. Therefore, it is possible to investigate preferred locations of the solvated electron and their correlation with its size and binding energy. At the same time, such a cluster is small enough to allow for a statistically converged dynamical description of the solvated electron using adequate DFT methods.

A typical computational setup for our *ab initio* molecular dynamics (AIMD) simulations for anionic clusters consisting of 32 water molecules is as follows (for more details see Refs. (21, 22, 36, 37)). Energies and forces are evaluated using the Becke, Lee, Yang and Parr (BLYP) exchange-correlation functional, with dispersion interactions accounted for using empirical pairwise damped London terms.(40) Self-interaction error is corrected by augmenting the BLYP functional with an additional term depending on the electron density of the unpaired electron within the restricted open-shell formulation of DFT.(41) The Kohn-Sham orbitals are expanded into an atom-centered triple-zeta basis set with two polarization functions, optimized for condensed molecular systems (molopt-TZV2P),(42) augmented by an additional grid of up to 1000 space-fixed Gaussian

functions. An auxiliary plane wave basis with a cutoff of 280 Ry is used for the electronic density. The Goedecker-Teter-Hutter norm-conserving pseudopotentials(43) are employed. The cluster is placed in a  $20 \times 20 \times 20 \text{ \AA}^3$  box and an open boundary conditions Poisson solver is used.(44) Classical equations of motion for the nuclei are propagated with a time step of 0.5 fs with initial conditions sampled from thermal distribution at the desired temperature and with no subsequent temperature coupling. All calculations are performed using the Quickstep module of the CP2K program package.(45)

Vertical detachment energy (VDE) of the electron, i.e., the negative of its vertical binding energy, is evaluated as the difference between ground state energies of the cluster before and after electron detachment, in the geometry of the anion. Within the restricted open-shell formalism the total spin density of the system coincides with the density of the singly occupied molecular orbital. Two important observables are the first and second moments of the spin distribution. The first moment  $\mathbf{r}_c$  provides the center of the spin distribution. The second moment corresponds to the gyration tensor, of which we monitor the trace – the radius of gyration  $r_g$ , and the relative shape anisotropy  $\kappa$ .(22)

### **3. Structural aspects of hydrated electrons**

The structure of an excess electron equilibrated in a liquid 32 water cluster at 300 K is presented in Figure 1A.(21) Simply scrutinizing the snapshot, which displays the water molecules and the unpaired spin density corresponding to the excess electron at three different isodensity values(22) leads to the conclusion that the electron occupies a cavity at the exterior region of the cluster. However, this cavity is quantitatively different from that

formed by atomic anions. In both cases the water cavity is polarized, with water molecules pointing one of their hydrogen atoms inside. However, since the excess electron density is “softer” than that of negative ions due to the lack of a positive nucleus, it more readily deforms from the spherical shape and water molecules can penetrate deeper into it. This is also seen from the radial density of the excess electron and the positions of the water molecules (Figure 1A), where there is sizable overlap between the solvated electron and the nearest ~4 water molecules. When the excess electron is attached to a cold amorphous solid 32 water cluster at 30-50 K the situation is very different.(21, 22) The electron slightly reorients water molecules at the surface of the cluster, however, a cavity cannot be formed at these cryogenic conditions. The result is a rather surface-delocalized “cushion-like” excess electron at the periphery of the cluster (Figure 1B).

The statistically averaged (over 25 ps equilibrium trajectory at 300 K) structure of the excess electron cavity and its radial density at ambient conditions is depicted in Figure 2. These plots exemplify the overlap between the excess electron and the radial distributions of the hydrogen and oxygen atoms of the surrounding water molecules. The hydrogen distribution exhibits a peak ~1.2 Å from the center of the electron, followed by an oxygen peak around 2-3 Å. Due to limited statistics (particularly at small distances) these curves are rather noisy, nevertheless, there is a large degree of similarity with analogous distribution functions from a recent pseudopotential model interpreted as a non-cavity electron.(9) This is striking, since visual inspection and analysis of our spin densities present a rather convincing picture of an electron cavity, albeit a soft one, into which water molecules can easily penetrate.(21, 36)

Suggestions have been made in the literature that VDE of the electron can be related to its position with respect to the solvating water system.(14, 17) To a limited extent, this is substantiated. Namely, the “cushion-like” structures occurring in cryogenic clusters have small values of VDE and are always located at the exterior of the cluster.(14, 15, 21, 22) However, the situation concerning the more strongly bound structures, which appear both in cryogenic solids(14, 15) and in warmer aqueous systems(17-20) is more complicated. Our DFT calculations(21, 36), as well as earlier pseudopotential calculations (27, 46, 47) show that in general there is little correlation between VDE and position of the hydrated electron (Figure 3A) and that strongly bound hydrated electrons can be found both in the interior and within the aqueous interface. There is, however, a remarkable inverse correlation between the size of the excess electron and its VDE – the smaller the electron the more strongly bound it is (see Figure 3B and also Reference (48)). Both DFT and pseudopotential calculations thus indicate that photoelectron spectroscopy is a powerful tool for determining the size of the excess electron rather than its position.

#### **4. Dynamical aspects of hydrated electrons**

Electrons attached to neutral water clusters relax very differently at ambient conditions of 300 K and at cryogenic temperatures of 30-50 K. Figure 4A shows the time evolution of the radius of gyration of the excess electron for three different types of trajectories and Figure 4B depicts the corresponding time evolution of the VDEs. In green, a set of trajectories corresponding to electron attachment to liquid water clusters at 300 K is presented. Initially, the electron is rather delocalized and weakly bound since the neutral

cluster geometry is not particularly favorable for electron binding. However, the electron polarizes the surrounding aqueous environment very quickly, first rotating neighboring water molecules so that hydrogens point to it and second building a cavity in the hydrogen bonding structure of the cluster. As a result, its size shrinks, VDE increases and within  $\sim 1.5$  ps properties of an equilibrated solvated electron (red distributions in Figure 4) are reached. It should be noted that DFT is only able to describe relaxation on the electronic ground state surface of the system. This may not fully capture the localization process, particularly its early stages, when the nuclear and excess electron dynamics may be happening on a comparable timescale. Nevertheless, the simulated localization times are comparable to the experimentally observed picosecond timescale relaxation of the excess electron in water.<sup>(6)</sup>

The localization process of electrons attached to cold (30-50 K) neutral clusters is depicted in blue in Figure 4. The initial stage of electron localization is similar to that in ambient clusters, albeit a bit slower. Within the first picosecond the excess electron polarizes the surface water molecules and, as a result, it starts to shrink and becomes more strongly bound. While at ambient conditions the excess electron subsequently creates a cavity in the liquid water structure, this does not happen in the cold solid clusters. As a result, the electron remains trapped in metastable states less than half way from the initial condition to a fully localized structure. The situation is very different if the excess electron is first equilibrated at 300 K and then cooled to cryogenic conditions (cyan lines in Figure 4). Upon cooling to 30-50 K, the electron becomes even more strongly bound and smaller in size than at 300 K. During subsequent dynamics at low temperature virtually nothing happens with this structure. This indicates that strongly and weakly bound excess electrons

can coexist in ensembles of cryogenic clusters depending on their way of formation, as observed in the experiment.(14, 15)

The correlation between radius of gyration and VDE for the same data sets and using the same color coding as in Figure 4 is presented in Figure 5. The first thing to note is the very good overlap between the equilibrium points and data from localization trajectories at 300 K. The only part that is missing from the equilibrium data corresponds to the strongly delocalized and loosely bound structures from the onsets of the localization trajectories. This region is close to that explored during cold localization at 30-50 K, except that the latter exhibits even weaker electron binding. This corresponds to the exterior “cushion-like” states which form at the surface of cold clusters. On the other side of the distribution, large binding energies and small sizes are signatures of equilibrated and consequently quenched electrons (cyan).

## **5. Reactivity of hydrated electrons**

The excess electron in water is a chemically unstable entity which can react with various impurities and, very slowly, also with water itself.(4) An important quencher of the hydrated electron, in particular at acidic conditions, is the hydronium cation. The electron-proton reaction in water leading to formation of a hydrogen atom was shown experimentally to be slower than a purely diffusion limited process.(4, 49) Also, measurements in deuterated water indicated that the reaction is a proton-transfer to the solvated electron(49) rather than electron transfer to the hydronium cation connected with transient formation of a localized  $\text{H}_3\text{O}$  radical, as suggested earlier.(50) Note that the  $\text{H}_3\text{O}$

radical has also been invoked recently in rationalizing ground and excited state processes involving hydrated electrons.(51, 52) However, in these studies the key species is not a genuine radical with the spin localized at the H<sub>3</sub>O moiety but rather an H<sub>3</sub>O<sup>+</sup>...e<sup>-</sup><sub>aq</sub> solvent-separated pair.(51, 52)

We used AIMD to elucidate the detailed molecular mechanism of the electron-proton reaction in water. In order to prepare the reactants we first equilibrated a 32 water system with an added proton and iodide anion. The latter was then replaced by an excess electron, which filled the iodide cavity, and the course of the reaction was then monitored for a set of trajectories.(37) In Figure 6 we analyze four snapshots along one of the reactive trajectories. The first snapshot, from the beginning of the trajectory, corresponds to a solvated electron which is only weakly perturbed by the presence of the hydronium cation at a distance of 4-5 Å (compare to equilibrated solvated electron in Figure 1A). Subsequently, the proton moves close to the water shell around the excess electron (Figure 6B). However, it does not react immediately but rather moves around this shell by proton hopping for more than a picosecond, confirming that the electron-proton reaction in water is not diffusion limited. (4, 49) Only after a suitable perturbation in the solvent shell occurs or is induced by the proton (Figure 6C), the reaction takes place and a hydrogen atom is formed (Figure 6D). The simulations also clearly show that it is the proton which moves to the hydrated electron, having a lower effective mass in water, in accord with the experimentally suggested proton transfer mechanism.(49)

Does the proton have to wait for a perturbation of the solvent shell of the excess

electron or does it induce it? The answer is clear from Figure 7 which depicts the correlation between the radius of gyration of the excess electron and its relative shape anisotropy along three reactive trajectories (lines), compared to equilibrium simulation without the excess proton (dots). An equilibrated electron is only weakly asymmetric, except for instances when it is rather delocalized. These geometries are, however, not relevant for the reaction requiring simultaneous localization and distortion of the excess electron, which only happens in the presence of the hydronium cation. For a successful reaction it is necessary that one water molecule penetrates deep into the excess electron density and donates a proton, which then becomes the nucleus of the newly formed hydrogen atom. At the same time this donating water molecule acquires the excess proton, its integrity being preserved.

## **6. Method development**

From the methodological point of view, providing an accurate picture of the solvated electron is an interesting and open challenge. When one of the prime targets is the study of its reactivity in the bulk liquid, only electronic structure methods that are able to describe the dynamics of hundreds of atoms in periodic boundary conditions are ultimately suitable. However, several problems have to be solved in order to reliably describe the subtle balance between localized and delocalized electronic states.

Approximate variants of density functional theory, in particular the computationally efficient generalized gradient approximations (GGA) employed in our work, are known to suffer from the self-interaction error. This error, which is more severe for systems with unpaired electrons, tends to artificially delocalize electronic states. It can be partially

corrected for using a self-interaction correction (SIC) which, in a recent formulation, is only applied to the unpaired electron and scaled to reproduce benchmark results.<sup>(41)</sup> Depending on the parametrization (we mostly used the standard values of  $a=0.2$  and  $b=0$  (41)), the SIC causes an overestimation of the VDE, which is most likely caused by the imbalance introduced by applying this correction only to the anionic state in the VDE calculation. This, however, changes little on the fact that the description of the structure and dynamics of the hydrated electron should be improved by introducing the SIC. As a matter of fact, the effect of SIC on the structure and dynamics of the hydrated electron is modest, however, it becomes crucial for the description of its reactivity. E.g., the electron-proton reaction toward the hydrogen atom does not run in water with GGA functionals without SIC.<sup>(37)</sup>

A second important technical aspect is the choice of the basis set. In CP2K, one uses an auxiliary plane-wave basis set and a primary Gaussian basis set which has to be sufficiently flexible and diffuse. For example, localized interior states can be more easily described with an atom-centered basis than delocalized surface states, and as such will be favored unless a suitable basis is employed. Three basis sets have been tested. A split valence basis set with diffuse functions (aug-TZV2P), a molecularly optimized basis set which contracts diffuse primitives with tighter valence orbitals (molopt-TZV2P), and a combination of the molopt-TZV2P basis with a regular grid of Gaussian basis function. The latter two basis sets do not suffer from linear dependencies, and are thus more suitable and more efficient for MD simulations of large systems, especially in periodic boundary

conditions. However, only with the addition of the Gaussian grid functions within a 10-13 Å cutoff (500-750 basis functions) a faithful description (equivalent to the use of the aug-TZV2P basis) of the diffuse surface bound electron can be obtained.

In future work, we plan to extend our studies to the properties and reactivity of the electron in the aqueous bulk, and address new challenges which may arise there. The first challenge will be the significant size effects that can be expected for the simulation of charged species and estimating VDE in periodic boundary conditions. Also, investigating reactions of the solvated electron with radicals (rather than with a closed-shell hydronium cation) will introduce another level of complexity in the electronic structure. Indeed, these systems are open-shell singlet biradicals having a multi-configurational character. Since multi-configurational wavefunction approaches are currently computationally intractable for large systems, this calls for DFT functionals with terms specifically describing static correlation.

## **Conclusions**

We employed *ab initio* molecular dynamics to characterize the structure, dynamics, and reactivity of an excess electron solvated in water. Using a negatively charged 32 water cluster as a model system we reached the following principal conclusions:

i) At ambient conditions the excess electron resides in a cavity close to the surface of the cluster. This cavity is softer and more flexible than that around atomic anions and water molecules penetrate rather deep into it, underscoring the importance of all (valence) electron description of the system which includes exchange interactions.

ii) The process of electron attachment to a neutral water system and subsequent localization is very different at ambient vs. cryogenic conditions. In the former, liquid, system, the cluster quickly reaches an equilibrated structure which corresponds to a well localized and strongly bound solvated electron. However, in the latter, solid, system, the electron gets trapped in a metastable “cushion-like” state at the periphery of the cluster, which is more weakly bound. Strongly bound states are observed in the cryogenic solid only if initially prepared at ambient conditions and subsequently quenched. This rationalizes the observation of several isomers in cryogenic cluster experiments and raises a question mark over extrapolations of excess electron properties from these clusters to the liquid bulk.

iii) The electron-proton reaction in water, as the simplest example of chemical quenching of the solvated electron, is shown to be, unlike in the gas phase, a complex many-body process. Adding more detail to the general experimentally derived mechanism, we demonstrate that the reaction is not diffusion limited and it is a proton transfer rather than electron transfer process where a localized  $\text{H}_3\text{O}$  radical does not play a role of a key intermediate. The rate-limiting step of the reaction is a deformation of the excess electron induced by the hydronium cation within which a single water molecule penetrates deep into the electron cavity.

As a final note we mention that after submission of this paper a new AIMD study of an electron attached to a cluster containing 105 water molecules has been published.<sup>(53)</sup> Despite the fact that the system is almost three times bigger than that investigated in our

group (and the DFT method employed is similar but not identical) the results are qualitatively the same. Namely, the authors of the new study also found a stable localized cavity electron, the binding energy of which does not strongly depend on its position within the cluster, as well as a weakly bound delocalized electron, which is kinetically trapped at the cold cluster surface (see Figure 3 in Reference (53)). These findings, together with earlier pseudopotential calculations performed for large clusters and extended systems,(9, 23-28) support our claim, that the results for the 32 water cluster anion presented here have direct implications also for electron solvated in larger aqueous systems.

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## **Biographical information**

**Ondrej Marsalek** was born in 1981. In 2008, he received a master's degree in theoretical physics at the Faculty of Mathematics and Physics, Charles University in Prague. Since 2008, he has been a doctoral student in the group of Pavel Jungwirth at the Institute of Organic Chemistry and Biochemistry of the Academy of Sciences of the Czech Republic.

**Frank Uhlig** was born in 1985. He received a Bachelor of Science from the Faculty of Chemistry at the University of Leipzig in 2008 and a Master of Science at the same institution in 2010. He is currently a doctoral student in the group of Pavel Jungwirth at the Institute of Organic Chemistry and Biochemistry of the Academy of Sciences of the Czech Republic.

**Joost VandeVondele** was born in 1975. He obtained a degree in engineering physics at the University of Ghent in Belgium. He received his doctoral degree in natural sciences from the ETH Zurich. As a postdoctoral fellow at the universities of Zurich and Cambridge, he became one of the leading developers of the CP2K simulation package. His current research in the Institute of Physical Chemistry at the University of Zurich targets the development and application of new tools for accurate simulations of large and complex systems.

**Pavel Jungwirth** graduated in physics from the Charles University in Prague and completed his doctoral thesis in computational chemistry in 1993. In 1994-5 he was a

Golda Meir Fellow at the Hebrew University in Jerusalem and a postdoc at the University of California at Irvine. In 1995-2003 he was a research group leader at the Heyrovský Institute and in 2004 he moved with his group to the Institute of Organic Chemistry and Biochemistry of the Academy of Sciences in Prague. Since 2000 he is also an Associate Professor at the Charles University (full professor since 2011). In 2009 he was elected a member of the Learned Society of the Czech Republic. He has educated more than a dozen of PhD. and MS students in computational chemistry, focusing primarily on modeling of ions at biologically and atmospherically relevant aqueous interfaces.

**Figure captions:**

**Figure 1:** Snapshots and radial density of the excess electron as a function of the distance from its center averaged (green) and integrated (blue) over the angular variables for A) a configuration with a well-developed cavity taken from an equilibrium simulation at  $T = 300$  K and B) a configuration sampled soon after attachment to a cold (30 K) water cluster with the electron on the surface of the cluster in a cushion-like state. Dashed vertical line shows the radius of gyration of the electron. Red and white dots show the positions of the oxygen and hydrogen atoms, respectively.

**Figure 2:** Radial density of the excess electron averaged over the angular variables (green) and radial distribution function of water oxygen (red) and hydrogen (black) atoms relative to the center of the excess electron from equilibrium configurations at  $T=300$  K.

**Figure 3:** A) Lack of correlation between vertical detachment energy of the excess electron and its distance from the cluster (measured in two different ways) and B) correlation between vertical detachment energy of the excess electron and its radius of gyration, both for equilibrium configurations at  $T=300$  K. In A) data using the average distance of the electron from the cluster center of mass are shown in green, whereas those using the distance between the center of the electron and the cluster center of mass are shown in blue.

**Figure 4:** Time evolution of A) radius of gyration and B) vertical detachment energy of the excess electron for different simulation setups, together with the equilibrium distribution at

T = 300 K (red). Simulations following electron attachment to cold (30-50 K) water clusters are shown in blue (8 trajectories). Simulations following electron attachment to water clusters at T = 300 K are shown in green (6 trajectories) and their average in black. Simulations of cold (30-50 K) anionic clusters with a pre-formed cavity are shown in cyan (2 trajectories).

**Figure 5:** Correlation between vertical detachment energy of the excess electron and its radius of gyration for different simulation setups. Simulations following electron attachment to cold (30-50 K) water clusters are shown in blue (8 trajectories). Simulations following electron attachment to water clusters at T = 300 K are shown in green (6 trajectories). Simulations of cold (30-50 K) anionic clusters with a preformed cavity are shown in cyan (2 trajectories). Equilibrium simulations of anionic clusters at T = 300 K are shown in red.

**Figure 6:** Radial density of the excess electron as a function of the distance from its center averaged (green) and integrated (blue) over the angular variables for configurations along a reactive trajectory. Dashed vertical line shows the radius of gyration of the electron. Red and white dots show the positions of the water oxygen and hydrogen atoms.

**Figure 7:** Correlation between radius of gyration and relative shape anisotropy of the excess electron for three reactive trajectories. Data from equilibrium simulations of the anionic cluster (i.e., without the excess proton) are shown for reference in gray.



Figure 1

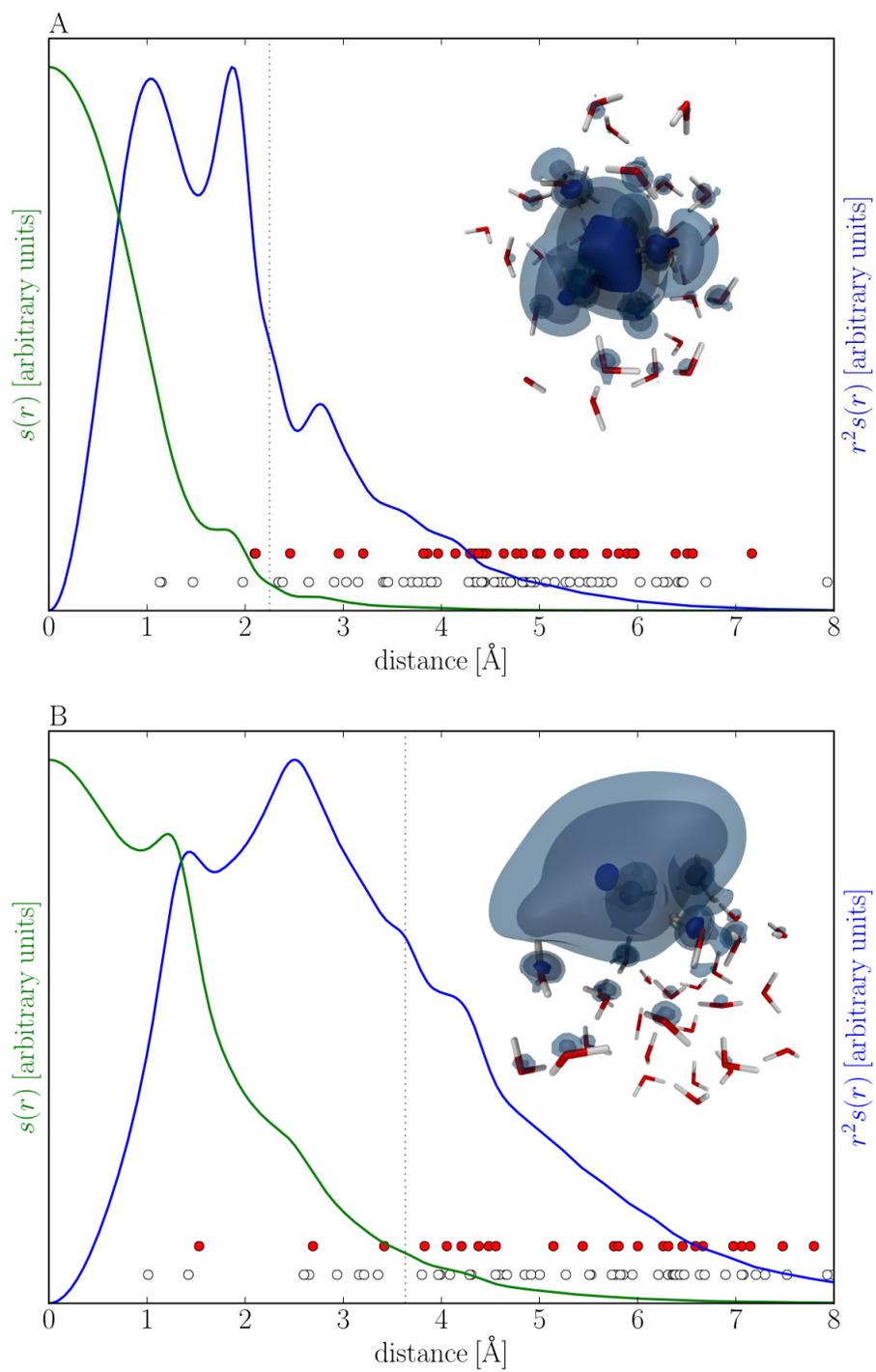


Figure 2

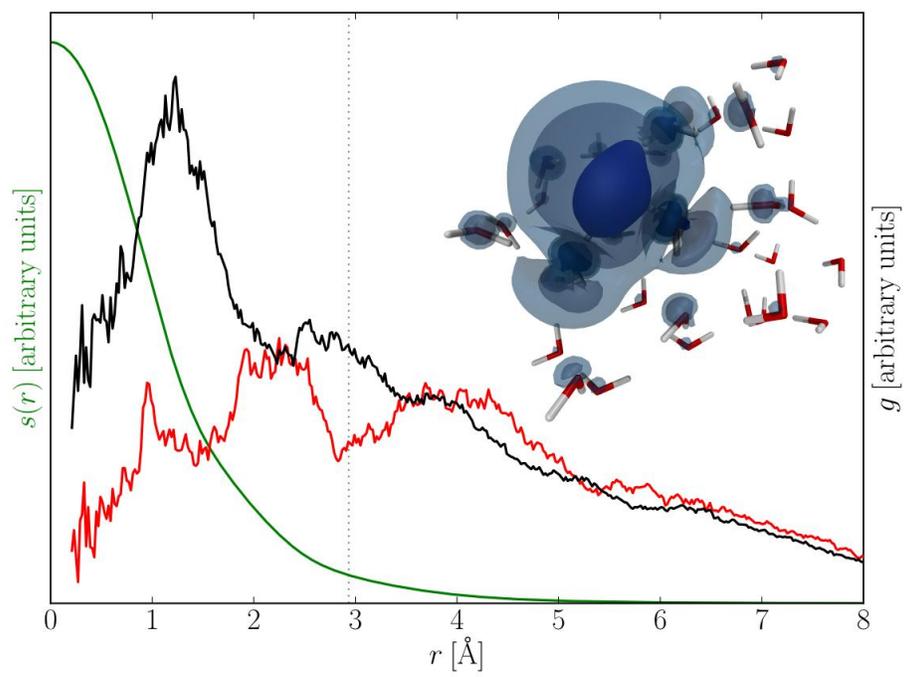


Figure 3

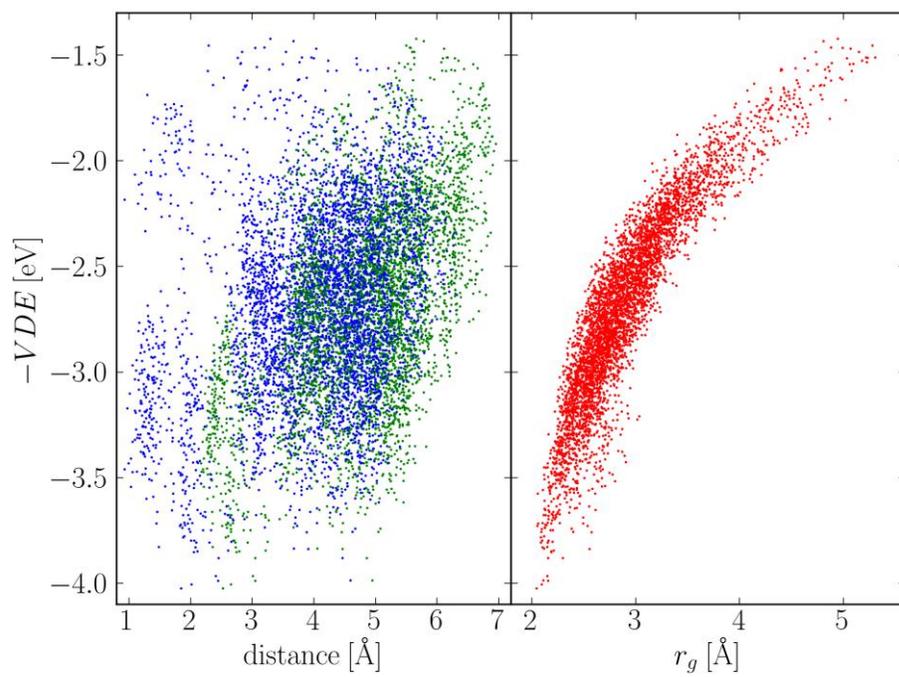


Figure 4

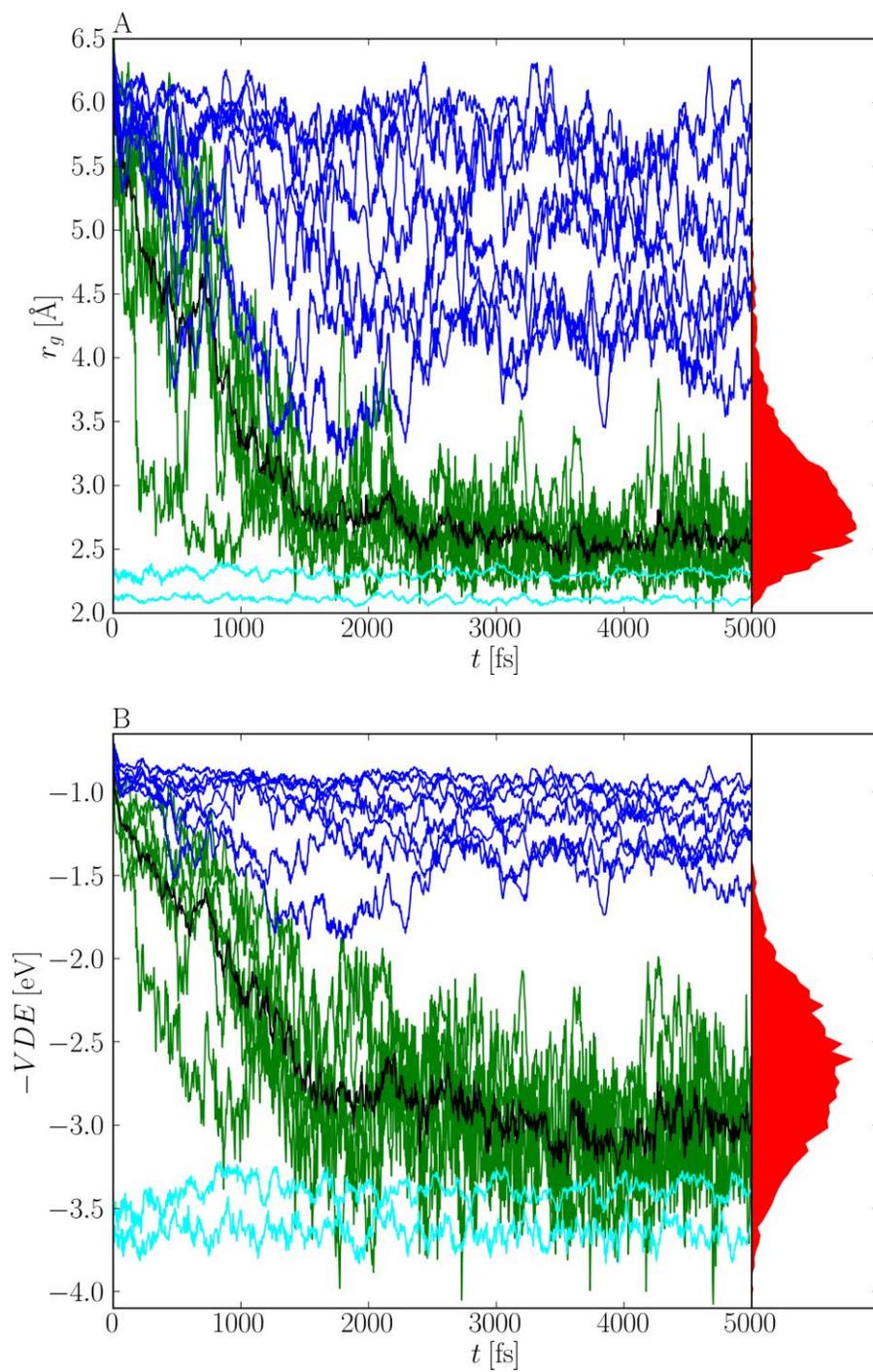


Figure 5

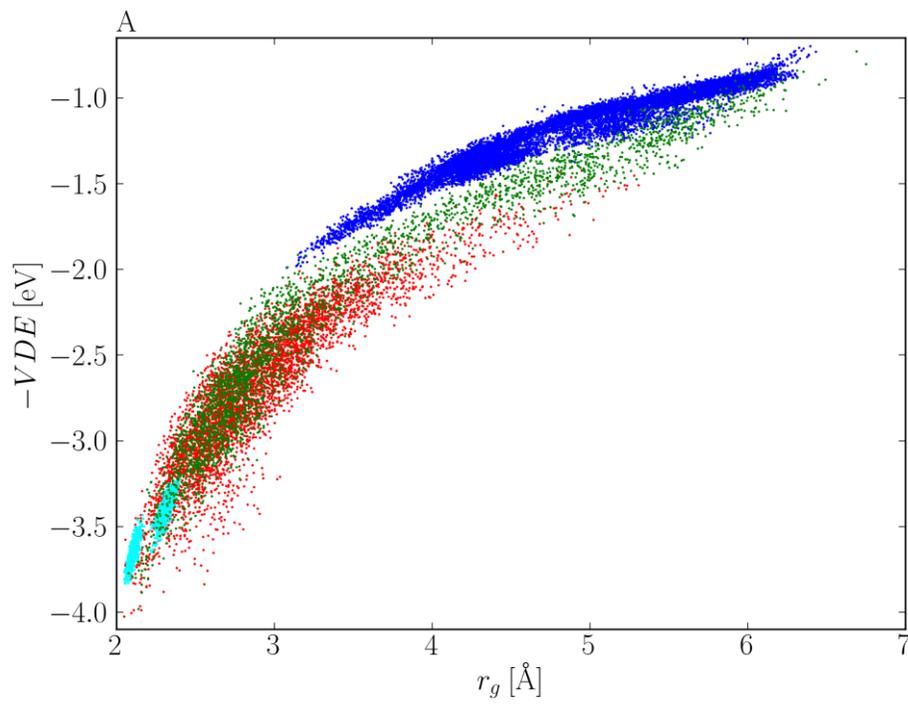


Figure 6

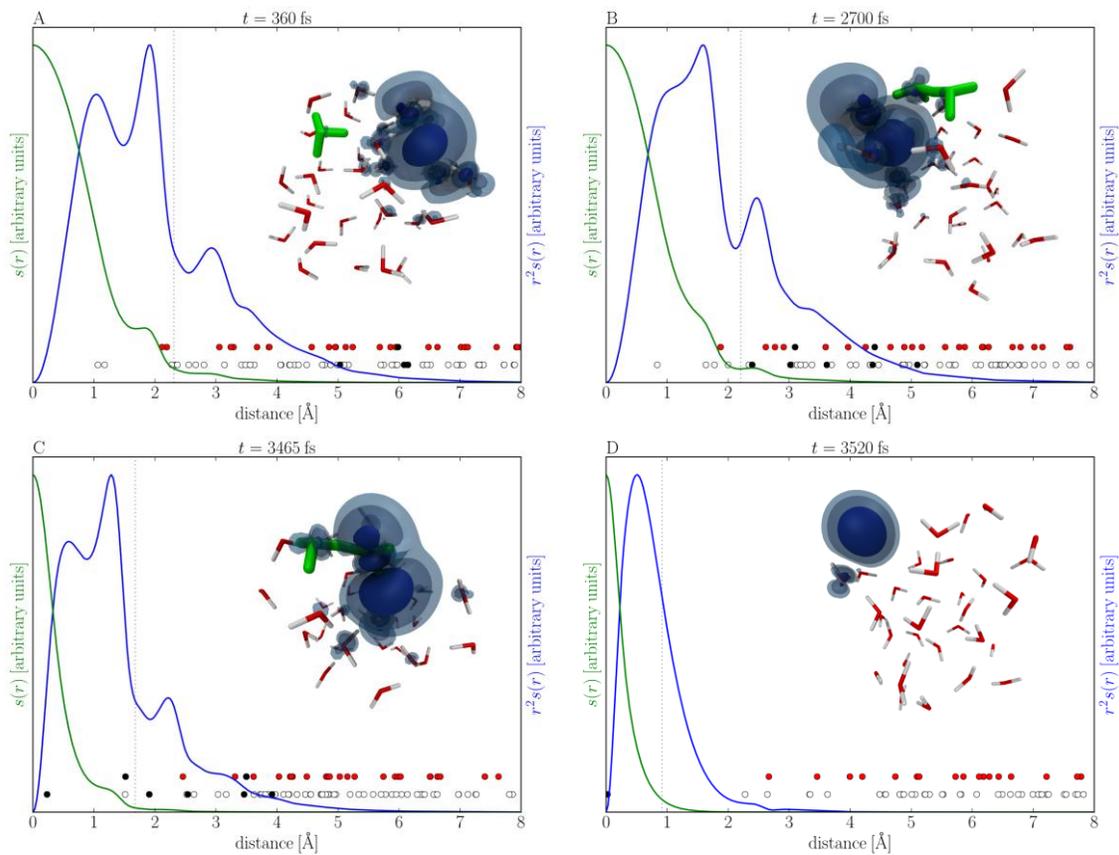
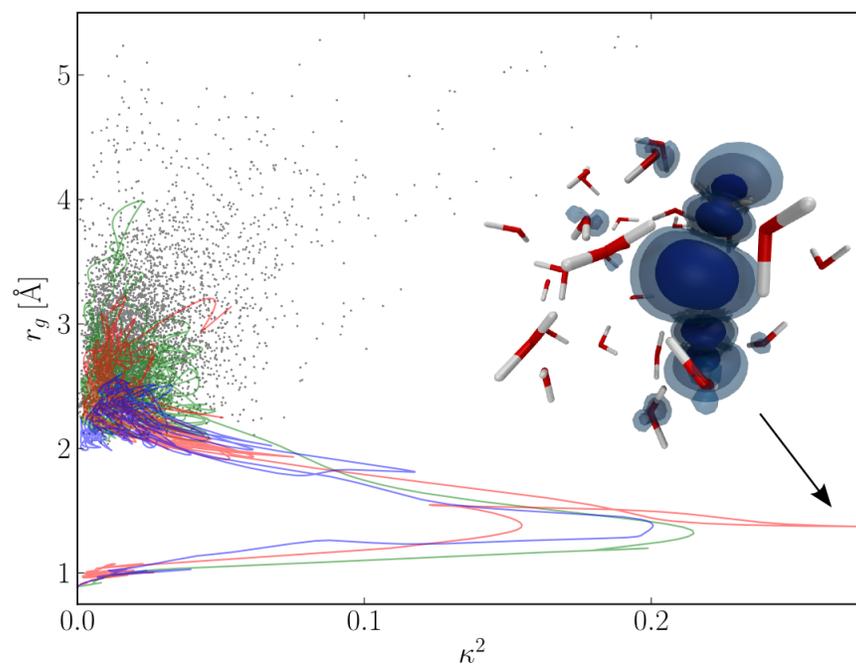
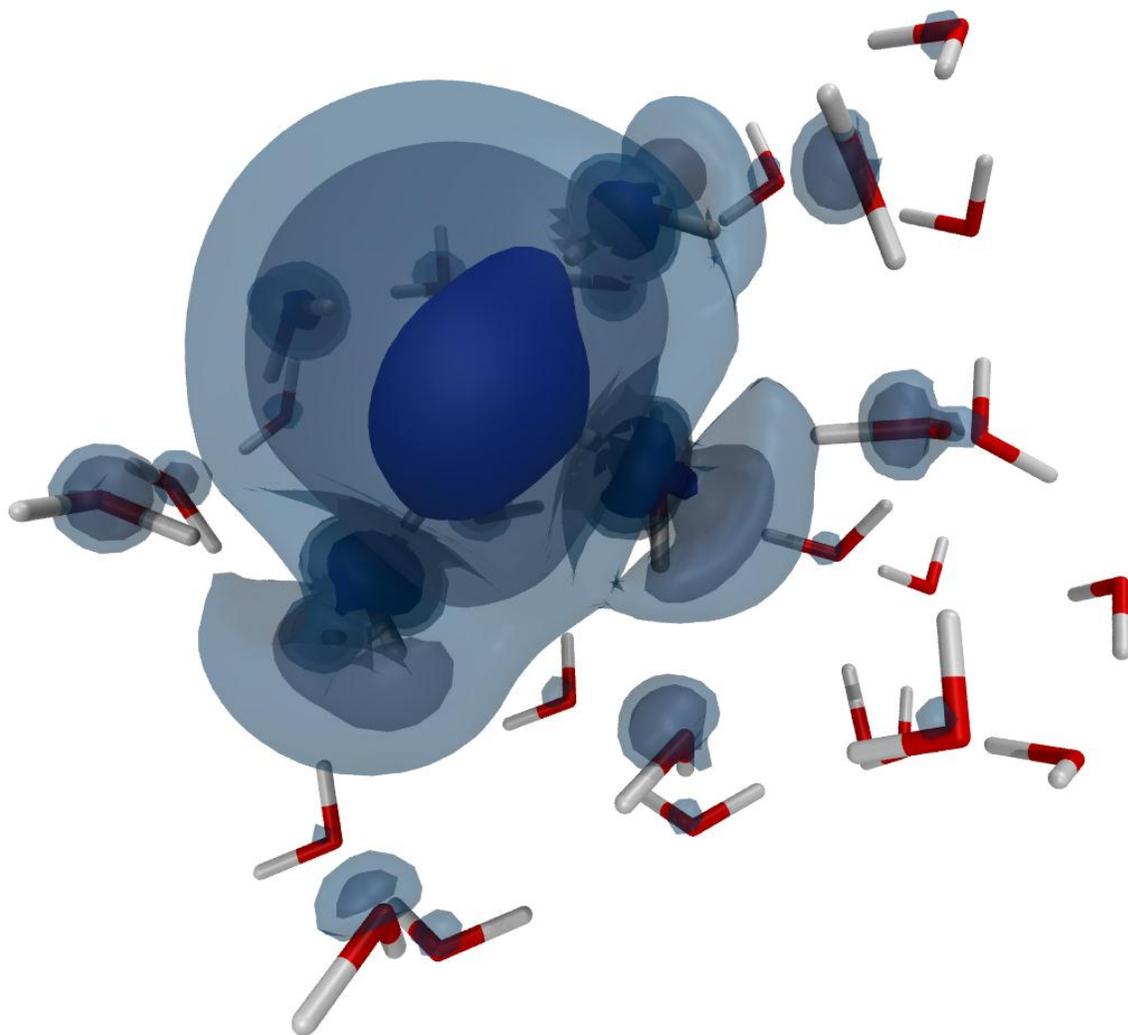


Figure 7



Conspectus graphics



## References

1. Gibson, G. E., and Argo, W. L. (1918) THE ABSORPTION SPECTRA OF THE BLUE SOLUTIONS OF CERTAIN ALKALI AND ALKALINE EARTH METALS IN LIQUID AMMONIA AND IN METHYLAMINE, *Journal of the American Chemical Society* 40, 1327-1361.
2. Cotton, F. A., and Wilkinson, G. (1988) *Advanced Inorganic Chemistry*, John Wiley & Sons, New York.
3. Hart, E. J., and Boag, J. W. (1962) ABSORPTION SPECTRUM OF HYDRATED ELECTRON IN WATER AND IN AQUEOUS SOLUTIONS, *Journal of the American Chemical Society* 84, 4090-4095.
4. Garrett, B. C. e. a. (2005) Role of water in electron-initiated processes and radical chemistry: Issues and scientific advances, *Chemical Reviews* 105, 355-389.
5. Bartels, D. M., Cook, A. R., Mudaliar, M., and Jonah, C. D. (2000) Spur decay of the solvated electron in picosecond radiolysis measured with time-correlated absorption spectroscopy, *Journal of Physical Chemistry A* 104, 1686-1691.
6. Kambhampati, P., Son, D. H., Kee, T. W., and Barbara, P. F. (2002) Solvation dynamics of the hydrated electron depends on its initial degree of electron delocalization, *Journal of Physical Chemistry A* 106, 2374-2378.
7. Chen, X. Y., and Bradforth, S. E. (2008) The ultrafast dynamics of photodetachment, *Annual Review of Physical Chemistry* 59, 203-231.
8. Shkrob, I. A. (2007) The structure of the hydrated electron. Part 1. Magnetic resonance of internally trapping water anions: A density functional theory study, *Journal of Physical Chemistry A* 111, 5223-5231.
9. Larsen, R. E., Glover, W. J., and Schwartz, B. J. (2010) Does the Hydrated Electron Occupy a Cavity?, *Science* 329, 65-69.
10. Turi, L., and Madarasz, A. (2011) Comment on "Does the Hydrated Electron Occupy a Cavity?", *Science* 331, 1387-c.
11. Jacobson, L. D., and Herbert, J. M. (2011) Comment on "Does the Hydrated Electron Occupy a Cavity?", *Science* 331, 1387-d.
12. Coe, J. V., Lee, G. H., Eaton, J. G., Arnold, S. T., Sarkas, H. W., Bowen, K. H., Ludewigt, C., Haberland, H., and Worsnop, D. R. (1990) Photoelectron-Spectroscopy of Hydrated Electron Cluster Anions, (H<sub>2</sub>O)<sub>N</sub>-=2-69, *Journal of*

*Chemical Physics* 92, 3980-3982.

13. Hammer, N. I., Shin, J. W., Headrick, J. M., Diken, E. G., Roscioli, J. R., Weddle, G. H., and Johnson, M. A. (2004) How do small water clusters bind an excess electron?, *Science* 306, 675-679.
14. Verlet, J. R. R., Bragg, A. E., Kammrath, A., Cheshnovsky, O., and Neumark, D. M. (2005) Observation of large water-cluster anions with surface-bound excess electrons, *Science* 307, 93-96.
15. Ma, L., Majer, K., Chirof, F., and von Issendorff, B. (2009) Low temperature photoelectron spectra of water cluster anions, *Journal of Chemical Physics* 131, 144303.
16. Sommerfeld, T., and Jordan, K. D. (2006) Electron binding motifs of (H<sub>2</sub>O)<sub>(n)</sub>(-) clusters, *Journal of the American Chemical Society* 128, 5828-5833.
17. Siefertmann, K. R., Liu, Y. X., Lugovoy, E., Link, O., Faubel, M., Buck, U., Winter, B., and Abel, B. (2010) Binding energies, lifetimes and implications of bulk and interface solvated electrons in water, *Nature Chemistry* 2, 274-279.
18. Shreve, A. T., Yen, T. A., and Neumark, D. M. (2010) Photoelectron spectroscopy of hydrated electrons, *Chemical Physics Letters* 493, 216-219.
19. Tang, Y., Shen, H., Sekiguchi, K., Kurahashi, N., Mizuno, T., Suzuki, Y. I., and Suzuki, T. (2010) Direct measurement of vertical binding energy of a hydrated electron, *Physical Chemistry Chemical Physics* 12, 3653-3655.
20. Sagar, D. M., Bain, C. D., and Verlet, J. R. R. (2010) Hydrated Electrons at the Water/Air Interface, *Journal of the American Chemical Society* 132, 6917-6919.
21. Marsalek, O., Uhlig, F., Frigato, T., Schmidt, B., and Jungwirth, P. (2010) Dynamics of Electron Localization in Warm versus Cold Water Clusters, *Physical Review Letters* 105, 043002.
22. Marsalek, O., Uhlig, F., and P., J. (2010) Electrons in Cold Water Clusters: An ab Initio Molecular Dynamics Study of Localization and Metastable States, *Journal of Physical Chemistry* 114, 20489-20495.
23. Barnett, R. N., Landman, U., Cleveland, C. L., and Jortner, J. (1988) ELECTRON LOCALIZATION IN WATER CLUSTERS .1. ELECTRON-WATER PSEUDOPOTENTIAL, *Journal of Chemical Physics* 88, 4421-4428.
24. Barnett, R. N., Landman, U., Cleveland, C. L., and Jortner, J. (1988) ELECTRON LOCALIZATION IN WATER CLUSTERS .2. SURFACE AND INTERNAL STATES, *Journal of Chemical Physics* 88, 4429-4447.

25. Barnett, R. N., Landman, U., Scharf, D., and Jortner, J. (1989) Surface and Internal Excess Electron-States in Molecular Clusters, *Accounts of Chemical Research* 22, 350-357.
26. Nicolas, C., Boutin, A., Levy, B., and Borgis, D. (2003) Molecular simulation of a hydrated electron at different thermodynamic state points, *Journal of Chemical Physics* 118, 9689-9696.
27. Turi, L., Sheu, W. S., and Rossky, P. J. (2005) Characterization of excess electrons in water-cluster anions by quantum simulations, *Science* 309, 914-917.
28. Sommerfeld, T., DeFusco, A., and Jordan, K. D. (2008) Model Potential Approaches for Describing the Interaction of Excess Electrons with Water Clusters: Incorporation of Long-Range Correlation Effects, *Journal of Physical Chemistry A* 112, 11021-11035.
29. Jacobson, L. D., and Herbert, J. M. (2010) A one-electron model for the aqueous electron that includes many-body electron-water polarization: Bulk equilibrium structure, vertical electron binding energy, and optical absorption spectrum, *Journal of Chemical Physics* 133, 154506.
30. Madarasz, A., Rossky, P. J., and Turi, L. (2010) Response of Observables for Cold Anionic Water Clusters to Cluster Thermal History, *Journal of Physical Chemistry A* 114, 2331-2337.
31. Shkrob, I. A., Glover, W. J., Larsen, R. E., and Schwartz, B. J. (2007) The structure of the hydrated electron. Part 2. A mixed quantum/classical molecular dynamics embedded cluster density functional theory: Single-excitation configuration interaction study, *Journal of Physical Chemistry A* 111, 5232-5243.
32. Herbert, J. M., and Head-Gordon, M. (2006) First-principles, quantum-mechanical simulations of electron solvation by a water cluster, *Proceedings of the National Academy of Sciences of the United States of America* 103, 14282-14287.
33. Xu, J., and Jordan, K. D. (2010) Application of the Diffusion Monte Carlo Method to the Binding of Excess Electrons to Water Clusters, *Journal of Physical Chemistry A* 114, 1364-1366.
34. Boero, M. (2007) Excess electron in water at different thermodynamic conditions, *Journal of Physical Chemistry A* 111, 12248-12256.
35. Renault, J. P., Vuilleumier, R., and Pommeret, S. (2008) Hydrated electron production by reaction of hydrogen atoms with hydroxide ions: A first-principles molecular dynamics study, *Journal of Physical Chemistry A* 112, 7027-7034.
36. Frigato, T., VandeVondele, J., Schmidt, B., Schutte, C., and Jungwirth, P. (2008)

- Ab initio molecular dynamics simulation of a medium-sized water cluster anion: From an interior to a surface-located excess electron via a delocalized state, *Journal of Physical Chemistry A* 112, 6125-6133.
37. Marsalek, O., Frigato, T., VandeVondele, J., Bradforth, S. E., Schmidt, B., Schutte, C., and Jungwirth, P. (2010) Hydrogen Forms in Water by Proton Transfer to a Distorted Electron, *Journal of Physical Chemistry B* 114, 915-920.
  38. Boero, M., Parrinello, M., Terakura, K., Ikeshoji, T., and Liew, C. C. (2003) First-principles molecular-dynamics simulations of a hydrated electron in normal and supercritical water, *Physical Review Letters* 90, 226403.
  39. Herbert, J. M., and Head-Gordon, M. (2005) Calculation of electron detachment energies for water cluster anions: An appraisal of electronic structure methods, with application to  $(\text{H}_2\text{O})_{20}$  and  $(\text{H}_2\text{O})_{24}$ , *Journal of Physical Chemistry A* 109, 5217-5229.
  40. Grimme, S. (2006) Semiempirical GGA-type density functional constructed with a long-range dispersion correction, *Journal of Computational Chemistry* 27, 1787-1799.
  41. VandeVondele, J., and Sprik, M. (2005) A molecular dynamics study of the hydroxyl radical in solution applying self-interaction-corrected density functional methods, *Physical Chemistry Chemical Physics* 7, 1363-1367.
  42. VandeVondele, J., and Hutter, J. (2007) Gaussian basis sets for accurate calculations on molecular systems in gas and condensed phases, *Journal of Chemical Physics* 127, 114105.
  43. Goedecker, S., Teter, M., and Hutter, J. (1996) Separable dual-space Gaussian pseudopotentials, *Physical Review B* 54, 1703-1710.
  44. Genovese, L., Deutsch, T., Neelov, A., Goedecker, S., and Beylkin, G. (2006) Efficient solution of Poisson's equation with free boundary conditions, *Journal of Chemical Physics* 125, 074105.
  45. VandeVondele, J., Krack, M., Mohamed, F., Parrinello, M., Chassaing, T., and Hutter, J. (2005) QUICKSTEP: Fast and accurate density functional calculations using a mixed Gaussian and plane waves approach, *Computer Physics Communications* 167, 103-128.
  46. Bartels, D. M. (2001) Moment analysis of hydrated electron cluster spectra: Surface or internal states?, *Journal of Chemical Physics* 115, 4404-4405.
  47. Madarasz, A., Rossky, P. J., and Turi, L. (2009) Interior- and surface-bound excess electron states in large water cluster anions, *Journal of Chemical Physics* 130,

124319.

48. Turi, L., Madarasz, A., and Rossky, P. J. (2006) Excess electron localization sites in neutral water clusters, *Journal of Chemical Physics* 125.
49. Han, P., and Bartels, D. M. (1992) H/D Isotope Effects in Water Radiolysis .4. the Mechanism of (H)Aq $\leftrightarrow$ (e-)Aq Interconversion, *Journal of Physical Chemistry* 96, 4899-4906.
50. Hart, E., and Anbar, M. (1970) *The hydrated electron*, Wiley-Interscience, New York.
51. Sobolewski, A. L., and Domcke, W. (2007) Computational studies of aqueous-phase photochemistry and the hydrated electron in finite-size clusters, *Physical Chemistry Chemical Physics* 9, 3818-3829.
52. Poterya, V., Fedor, J., Pysanenko, A., Tkac, O., Lengyel, J., Oncak, M., Slavicek, P., and Farnik, M. (2011) Photochemistry of HI on argon and water nanoparticles: Hydronium radical generation in HI(H<sub>2</sub>O)<sub>n</sub>, *Physical Chemistry Chemical Physics* 13, 2250–2258.
53. Barnett, R. N., Giniger, R., and Cheshnovsky, O. (2011) Dielectron attachment and hydrogen evolution reaction in water clusters, *Journal of Physical Chemistry A* 115, 7378-7391.