

# Hydrated Electrons in High-Concentration Electrolytes Interact with Multiple Cations: A Simulation Study

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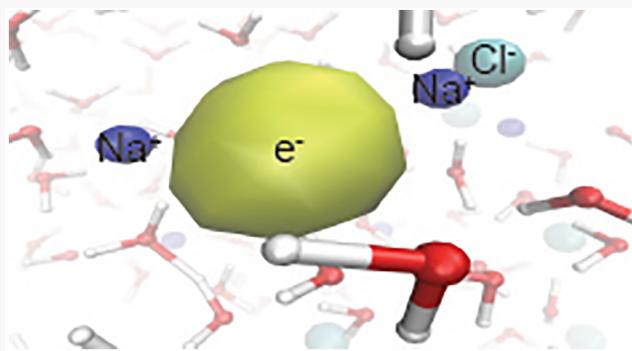
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**ABSTRACT:** Experimental studies have demonstrated that the hydrated electron's absorption spectrum undergoes a concentration-dependent blue-shift in the presence of electrolytes such as NaCl. The blue-shift increases roughly linearly at low salt concentration but saturates as the solubility limit of the salt is approached. Previous attempts to understand the origin of the concentration-dependent spectral shift using molecular simulation have only examined the interaction between the hydrated electron and a single sodium cation, and these simulations predicted a spectral blue-shift that was an order of magnitude larger than that seen experimentally. Thus, in this paper, we first explore the reasons for the exaggerated spectral blue-shift when a simulated hydrated electron interacts with a single  $\text{Na}^+$ . We find that the issue arises from nonpairwise additivity of the  $\text{Na}^+ - \text{e}^-$  and  $\text{H}_2\text{O} - \text{e}^-$  pseudopotentials used in the simulation. This effect arises because the solvating water molecules donate charge into the empty orbitals of  $\text{Na}^+$ , lowering the effective charge of the cation and thus reducing the excess electron–cation interaction. Careful analysis shows, however, that although this nonpairwise additivity changes the energetics of the electron– $\text{Na}^+$  interaction, the forces between the electron,  $\text{Na}^+$ , and water are unaffected, so that mixed quantum/classical (MQC) simulations produce the correct structure and dynamics. With this in hand, we then use MQC simulations to explore the behavior of the hydrated electron as an explicit function of NaCl salt concentration. We find that the simulations correctly reproduce the observed experimental spectral shifting behavior. The reason for the spectral shift is that as the electrolyte concentration increases, the average number of cations simultaneously interacting in contact pairs with the hydrated electron increases from 1.0 at low concentrations to  $\sim 2.5$  near the saturation limit. As the number of cations that interact with the electron increases, the cation/electron interactions becomes slightly weaker, so that the corresponding  $\text{Na}^+ - \text{e}^-$  distance increases with increasing salt concentration. We also find that the dielectric constant of the solution plays little role in the observed spectroscopy, so that the electrolyte-dependent spectral shifts of the hydrated electron are directly related to the concentration-dependent number of closely interacting cations.



## INTRODUCTION

As the paradigm quantum mechanical solute, the hydrated electron has been the subject of much interest since it was first observed nearly six decades ago.<sup>1</sup> Indeed, the scientific community has worked hard to develop theoretical models<sup>2–6</sup> and perform *ab initio* simulations<sup>7–12</sup> that can explain the experimentally observed properties of this deceptively simple object. Despite all this effort, however, there are still several features of the hydrated electron's behavior that lack molecular understanding. These include the fact that the hydrated electron's absorption spectrum red-shifts with temperature by  $\sim 2.2$  meV/K, independent of the solvent density;<sup>13</sup> the fact that spectral moment analysis shows that the hydrated electron's radius of gyration increases with increasing temperature,<sup>14</sup> but the electron's molar solvation volume is essentially temperature independent;<sup>15</sup> and the fact that the addition of electrolytes causes a blue-shift of the hydrated electron's absorption spectrum.<sup>16</sup>

One of the more interesting aspects of the behavior of hydrated electrons in the presence of electrolytes is that other than the spectral shift to higher energies, the electron's absorption spectrum does not seem to appreciably change shape.<sup>16–19</sup> In general, di- and trivalent cations produce larger spectral blue-shifts than monovalent cations, and perchlorate salts yield larger blue-shifts than chloride-based electrolytes with the same cations.<sup>16</sup> The magnitude of the observed blue-shift of the hydrated electron's absorption spectrum increases with increasing salt concentration, but the blue-shift appears to

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saturate as the amount of added salt approaches its solubility limit.<sup>16</sup> This leaves open the question of what causes the salt-induced spectral blue-shift: does it result from a change in the average distance between the hydrated electron and the surrounding cations, the fact that electrolytes increase the dielectric constant of the solution, the formation of stable cation–electron contact pairs, or some combination of all of these? Answering these questions forms the motivation for this study, in which we examine the behavior of hydrated electrons in the presence of different concentrations of NaCl via molecular simulation.

To date, there is relatively little simulation work in the literature focused at understanding the behavior of hydrated electrons in the presence of dissolved salts.<sup>20–22</sup> The reason for this is that such simulations are computationally quite expensive. To simulate aqueous solutions with salt concentrations of a few molal, tens of salt molecules and hundreds of water molecules are required at the very minimum. Moreover, aqueous electrolyte solutions are known to relax quite slowly due to Coulombic correlations and the need for ions to undergo translational diffusion. Thus, the required simulation size and time scales put *ab initio* calculations out of reach, even with density functional theory (DFT), particularly if one wants to do importance sampling. Thus, the fact that the electron must be treated quantum mechanically leaves mixed quantum/classical (MQC) methods as the only current computationally feasible approach.

Of the few attempts to study this problem via MQC simulation, Boutin and co-workers elected to study a simplified system consisting of a hydrated electron in the presence of a single sodium cation at room temperature.<sup>21</sup> The fact that there was only a single cation allowed these researchers to construct the cation–electron potential of mean force (PMF) using the sum-over-states quantum umbrella sampling (SOS-QUS) approach developed by Borgis and Staib.<sup>23</sup> Boutin and co-workers concluded that the formation of a cation–electron contact pair (CP) was thermodynamically favored and suggested that the reason for the increased spectral shift at higher salt concentrations was due to a decrease in the average cation–electron distance. However, when these workers examined the properties of the stable ( $\text{Na}^+$ ,  $\text{e}^-$ ) simulated contact pair, they calculated a spectral blue-shift that was nearly an order of magnitude larger than that observed experimentally.<sup>20,21</sup>

Recently, we revisited MQC simulations of single ( $\text{Na}^+$ ,  $\text{e}^-$ ) contact pairs, focusing on how the choice of the classical cation–water interactions affects the quantum mechanical cation–electron PMF.<sup>22</sup> To perform this investigation, we used a quantum umbrella sampling technique based on the coupled-perturbed response equations (CP-QUS), which does not suffer from the convergence-related shortcomings of the SOS-QUS method.<sup>24</sup> We found that there exists a delicate balance between the way the cation is solvated and the  $\text{Na}^+$ – $\text{e}^-$  interaction: the stability of the ( $\text{Na}^+$ ,  $\text{e}^-$ ) CP decreases when the strength of interaction between the cation and water increases.<sup>22</sup> We also found, in agreement with the findings of Boutin and co-workers,<sup>20,21</sup> that the calculated spectral blue-shift of the CP was significantly exaggerated relative to experiment. However, we also saw that the spectral blue-shift did not depend monotonically on the cation–electron distance.<sup>22</sup> This means that the behavior of the hydrated electron with electrolyte concentration cannot be explained by

simply assuming the average cation–electron distance decreases as the amount of salt increases.

The purpose of this paper is twofold. First, we work to understand why MQC simulations predict a spectral blue-shift that is significantly larger than that seen experimentally. We find that the issue arises from nonpairwise additivity in the pseudopotentials employed to describe how the hydrated electron interacts with sodium cations that are solvated by water molecules. We also show that although our pairwise-additive calculations produce overly bound eigenenergies, the energy gradients (i.e., forces) calculated in the simulations match well with those computed when nonpairwise additivity is accounted for, so we can use the simulations along with an additional energy shift to provide physical insights into this system. Second, with this understanding in hand, we explore the behavior of hydrated electrons in the presence of different concentrations of NaCl via MQC molecular dynamics simulations. Our calculations include up to 30 NaCl and 500 water molecules to simulate electrolyte solutions with up to  $\sim 4$  *m* concentration. We find that the hydrated electron can form simultaneous contact pairs with up to three cations: the number of simultaneously paired cations increases with increasing electrolyte concentration. The spectrum of the hydrated electron undergoes an additional blue-shift with each paired cation, saturating once three cations are stably paired. When we study contact pairs with the same number of cations in solutions with different salt concentrations, we find that the effect of solution dielectric on the hydrated electron's spectrum is negligible. Overall, the molecular details of how hydrated electrons behave in the presence of electrolytes are extraordinarily rich and depend on the microscopic details of cation solvation, electron solvation, and multiple cation–electron ion pairing.

## METHODOLOGY

We used mixed quantum/classical molecular dynamics with Ewald long-range electrostatics to simulate an excess electron in aqueous NaCl solutions of 0.0, 1.0, and 3.8 *m* concentration as well as in a 0.1 *m* aqueous  $\text{Na}^+$  solution (with no  $\text{Cl}^-$  counterion) to investigate how salt concentration affects the properties of the hydrated electron. As summarized in Table 1, each simulation consisted of a cubic box with periodic boundary conditions filled with a varying number of classical flexible single-point-charge (SPC-flex)<sup>25</sup> water molecules, Lennard-Jones (LJ)-type classical ions,<sup>26</sup> and a single quantum mechanical electron represented in a basis of  $24 \times 24 \times 24$  plane waves.<sup>27</sup> The size of each simulation box was chosen to

**Table 1. Parameters for the Simulation Trajectories Studied in This Work<sup>a</sup>**

NaCl molality	water molecules	NaCl molecules	simulation box length (Å)	basis-set grid spacing (Å)
0.0	499	0	24.65	0.747
0.1 <sup>b</sup>	497	1	24.63	0.747
1.0	481	9	24.49	0.742
3.8	439	30	24.34	0.738

<sup>a</sup>The box size for each molality was chosen to match the experimental density at room temperature and pressure. The grid spacing corresponds to the cubic box spanned by the  $24 \times 24 \times 24$  plane wave basis for the quantum subsystem. <sup>b</sup>The chloride anion was not included in the 0.1 *m* simulation, which contained only a single sodium cation.

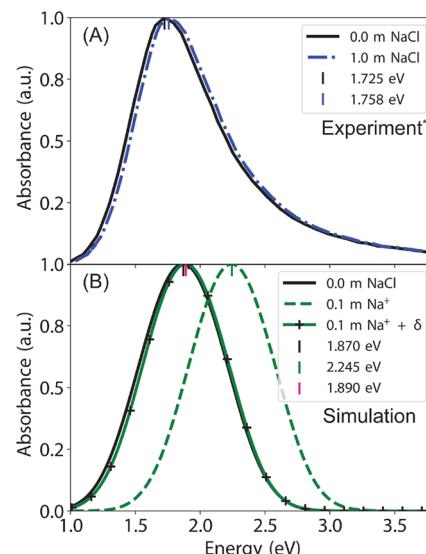
reproduce the experimental density of the electrolyte solution at room temperature and pressure, and the corresponding basis set spanned a cubic grid that occupied roughly 38% of the simulation box's volume. To ensure that the electron's wave function did not spill off the edge of the grid, the origin of the grid was recentered on the electron's center-of-mass (COM) every 100 fs. The water–electron interaction was described by using the cavity-forming pseudopotential developed by Turi and Borgis (TB),<sup>3</sup> and Phillips–Kleinman (PK) pseudopotentials based on the frozen core Hartree–Fock (HF) approximation were used to describe the interactions of the hydrated electron with both the sodium cations, taken from the literature,<sup>28,29</sup> and the chloride anions, developed newly for this work. Details of the pseudopotentials and classical force fields can be found in the *Supporting Information*.

Our initial configurations were obtained by running 400 ps long classical trajectories for the various aqueous NaCl solutions, without the quantum mechanical excess electron, in the microcanonical (NVE) ensemble at room temperature. For simulations including the hydrated electron, we extracted the final configurations from the all-classical trajectories and added the quantum mechanical electron as a negative net charge to the system in the lowest adiabatic eigenstate, running MQC dynamics in the NVE ensemble at  $\sim 298$  K for 240 ps; we allowed equilibration of the initially delocalized electron to occur for the initial 50 ps of dynamics and did not include this portion of the trajectories in our analyses. We used the velocity-Verlet algorithm with a 0.5 fs time step to propagate the MQC dynamics,<sup>30</sup> with the quantum mechanical forces evaluated via the Hellman–Feynman theorem.<sup>31</sup>

To compute the  $\text{Na}^+–\text{e}^-$  PMF for each of our simulated electrolyte solutions with the CP-QUS method,<sup>24</sup> we restrained the cation–electron center-of-mass distance of a single  $\text{Na}^+$  ion by applying a harmonic umbrella potential with a 1.5 eV/Å<sup>2</sup> force constant. A total of 15 25 ps long simulation windows in the canonical (NVT) ensemble were run as the targeted cation–electron distance was increased from 0 to 4 Å in 0.25 Å increments. Because the calculated PMFs appeared to have reached an asymptote by electron–cation separations of 4 Å, we ran only three additional simulation windows separated by 0.5 Å beyond this separation distance. The classical subsystem for these trajectories was propagated by using the velocity-Verlet algorithm with a 0.5 fs time step,<sup>30</sup> while the temperature was held constant at 298 K by using the Nosé–Hoover chain thermostat.<sup>32</sup> Uncorrelated configurations were extracted every 200 fs from the last 20 ps of each trajectory, and PMFs were constructed from the data by using the multistate Bennett acceptance ratio method (MBAR).<sup>33</sup>

## RESULTS AND DISCUSSION

**Pairwise-Additivity Limitations of Frozen-Core One-Electron Pseudopotentials for  $\text{Na}^+$  in Water.** In experimental studies of hydrated electrons in the presence of electrolytes, the main data collected is the absorption spectrum as a function of the identity and concentration of added salt. The black solid curve in Figure 1A shows the experimentally measured absorption spectrum of the hydrated electron at room temperature, while the blue dot-dashed curve shows the electron's spectrum in the presence of 1.0  $m$  NaCl; both spectra are reproduced from reported Gauss–Lorentz fits to the measured absorption line shape.<sup>16</sup> The experiment shows clearly that the spectrum of the hydrated electron changes relatively little in the presence of salt, with the main salt-



**Figure 1.** Experimental (A) and simulated (B) absorption spectra of the hydrated electron with and without the influence of added salt. In both panels, the black solid curve represents the spectrum of the hydrated electron in pure water. The blue dot-dashed curve in panel A shows the experimental spectrum in a 1.0  $m$  NaCl solution, which is blue-shifted from that in pure water by 33 meV. The green dashed curve in panel B shows the simulated spectrum of a hydrated electron interacting with a single  $\text{Na}^+$ ; the green solid curve with the cross markers is the same spectrum shifted by  $\delta_3 = 0.355$  eV to correct for nonpairwise additivity; see the text for details. \*Experimental data taken from the Gauss–Lorentz fits reported in ref 16.

dependent feature being a slight ( $\sim 33$  meV) overall blue-shift. The experiments by Bonin et al.<sup>16</sup> also suggest that the hydrated electron's spectrum does not show a salt-induced change in shape or width, only the small overall shift.

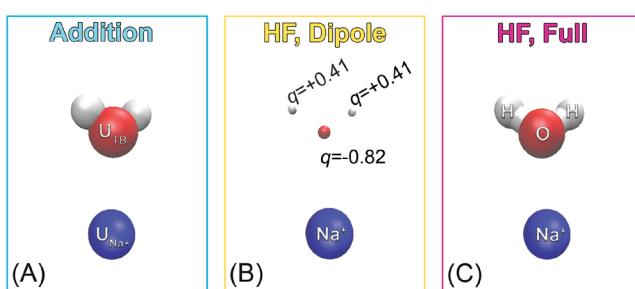
Figure 1B shows the calculated spectroscopy of the hydrated electron (represented with the Turi–Borgis pseudopotential<sup>3</sup>) both in neat water (black solid curve) and in the presence of a single sodium cation (green dashed curve). Although the simulations do predict a blue-shift of the electron's spectrum in the presence of salt, which is consistent with experiment, the magnitude of the simulated electron's spectral shift in the presence of  $\text{Na}^+$  ( $\sim 375$  meV) is an order of magnitude larger than that seen experimentally (as also seen in previous simulation work<sup>20–22</sup>). Thus, the first of the two main questions we wish to explore in this paper is why the salt-induced spectral blue-shift of the hydrated electron predicted by MQC calculations is so much larger than that seen experimentally?

The exaggerated spectral blue-shift seen with the MQC simulations is surprising given that the pseudopotentials used in this and previous simulation work were derived by using the Phillips–Kleinman (PK) formalism,<sup>34,35</sup> so they are based on quantum chemistry calculations and do not have adjustable parameters. In particular, the Turi–Borgis water–electron pseudopotential<sup>3</sup> replicates the absorption spectrum of the hydrated electron reasonably accurately (cf. the black curves in Figures 1A,B), and the  $\text{Na}^+–\text{e}^-$  pseudopotential matches all-electron calculations in terms of both the Na ionization energy and the position of the Na spectral D line.<sup>29</sup> Thus, the overly large blue-shift must arise from the way the two different pseudopotentials interact in the simulation.

In previous work, we saw that the frozen-core approximation inherent in the development of PK pseudopotentials could fail because the core orbitals used to calculate the pseudopotential can change in different environments.<sup>36</sup> This leads to the question of whether there might be a similar breakdown of the frozen core approximation for  $(\text{Na}^+, \text{e}^-)$  contact pairs that does not occur for either isolated  $\text{Na}^+$  ions or hydrated electrons and, if so, could such a breakdown could be responsible for the exaggerated calculated contact-pair spectral blue-shift. The  $\text{Na}^+ - \text{e}^-$  pseudopotential we use was derived in the gas phase, and it makes sense that an excess electron might interact with aqueous  $\text{Na}^+$  in a different way than with gas-phase  $\text{Na}^+$ . In particular, if the presence of water decreased the interaction between an excess electron and  $\text{Na}^+$  relative to that in the gas phase, then the electron in an aqueous  $(\text{Na}^+, \text{e}^-)$  contact pair would be overly bound, possibly explaining the exaggerated spectral blue-shift.

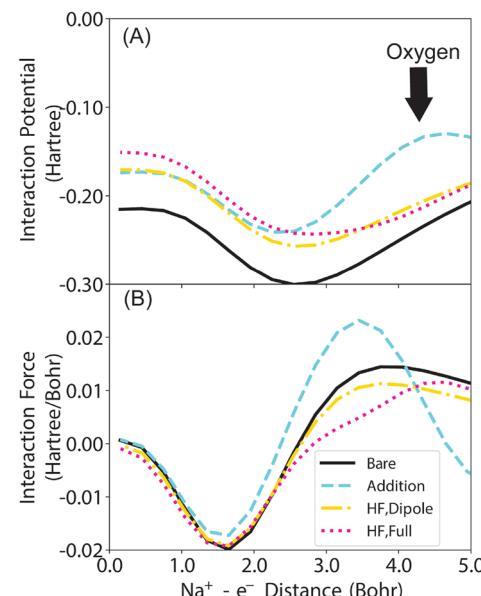
Here, we argue that there indeed is a significant change in the electronic structure of  $\text{Na}^+$  in the presence of water that can explain why MQC calculations with pairwise additive pseudopotentials yield an overly blue-shifted spectrum for aqueous electron–cation contact pairs. Several groups, using both *ab initio*<sup>37,38</sup> and polarizable classical MD methods,<sup>39</sup> have noted that when sodium cations are dissolved in water, the first solvation shell waters donate charge to the cation's empty 3s atomic orbital. The net result is that the effective charge on aqueous  $\text{Na}^+$  decreases from  $1.0e$  in the gas phase to  $\sim 0.9e$  in aqueous solution.<sup>39</sup> Thus, an aqueous sodium cation should be less attractive to an excess electron than a gas-phase  $\text{Na}^+$ . This effect is missing in our MQC simulations, which use only pairwise-additive pseudopotentials that do not account for this charge transfer.

To quantify how this charge transfer should affect the simulated  $\text{Na}^+ - \text{e}^-$  interaction in water, we performed a set of three quantum mechanical calculations describing how an excess electron interacts with a  $\text{Na}^+ : \text{H}_2\text{O}$  complex via a pseudopotential. In all three calculations, the water molecule is placed at the  $2.3 \text{ \AA} = 4.3 \text{ bohr}$  distance it is typically found next to  $\text{Na}^+$  in aqueous solution, with the O end of the molecule pointing toward the cation, as depicted in Figure 2. The three



**Figure 2.** Schematic of configurations used to calculate HF-based PK pseudopotentials to better understand how charge transfer between water and  $\text{Na}^+$  affects the interaction with an excess electron in MQC simulations at three distinct levels of theory. The first cation–water complex, seen in panel A, was described by the addition of separate  $\text{Na}^+ - \text{e}^-$  and  $\text{H}_2\text{O} - \text{e}^-$  pseudopotentials, as in the MQC trajectories. The second calculation, illustrated in panel B, used a  $\text{Na}^+ : \text{H}_2\text{O}$  complex constructed with a fully quantum mechanical  $\text{Na}^+$  interacting with the point charges of a classical SPC water molecule. The final calculation, depicted in panel C, developed a pseudopotential based on an all-electron  $\text{Na}^+ : \text{H}_2\text{O}$  structure.

calculations differ in how the electronic structure of the water is treated in deriving the pseudopotential, as described in more detail in the Supporting Information. In the first calculation, we used the sum of the  $\text{Na}^+ - \text{e}^-$  ( $U_{\text{Na}^+}$ ) and TB water–electron ( $U_{\text{TB}}$ ) pseudopotentials, the same as what was used in our MQC simulations (Figure 2A). The second calculation used the PK method to calculate a potential by using core orbitals determined from a Hartree–Fock (HF) calculation including all the electrons on the  $\text{Na}^+$  cation but with the water molecule represented only by the point charges used in the SPC model ( $U_{\text{HF,Dipole}}$  Figure 2B). Finally, we also derived a PK pseudopotential based on core orbitals from an HF calculation using all of the electrons on both the cation and the water ( $U_{\text{HF,Full}}$  Figure 2C). The three PK potentials derived this way are shown in Figure 3, and the corresponding electronic eigenvalues are summarized in Table 2.



**Figure 3.** (A) PK pseudopotentials, calculated as described in the Supporting Information for the three levels of theory depicted in Figure 2, for an excess electron interacting with  $\text{Na}^+$  (black curve) or a  $\text{Na}^+ : \text{H}_2\text{O}$  complex (various colored curves). The center of the  $\text{Na}^+$  cation is at the origin, and the center of the water O atom is located at 4.3 bohr. (B) Gradients of the potentials shown in panel A. The fact that the gradients are so similar in the attractive region where the electron resides suggests that the structures and dynamics produced in the MQC simulations are correct, even if the energetics are not (see Table 2).

Table 2 shows that the effect of charge transfer from water onto the sodium cation makes a substantial difference in the estimated eigenenergy of an excess electron interacting with aqueous  $\text{Na}^+$ . The computed eigenvalue of the pairwise

**Table 2. One-Electron Ground-State Eigenenergies Calculated by Using the PK Pseudopotentials Shown in Figure 3 for Excess Electrons Interacting with  $\text{Na}^+ : \text{H}_2\text{O}$  Complexes**

method	eigenenergy (eV)
$U_{\text{Addition}}$	-4.277
$U_{\text{HF,Dipole}}$	-4.273
$U_{\text{HF,Full}}$	-4.046

addition of separate cation–electron and water–electron pseudopotentials, as used in our simulations, is equivalent to an all-electron calculation on a  $\text{Na}^+$  ion that is perturbed by the dipole moment of an SPC water molecule. Because a water molecule sitting 2.3 Å away from a  $\text{Na}^+$  interacts with an excess electron primarily through electrostatics, the sum of individual pseudopotentials is indeed equivalent to treating the water only as a perturbing dipole, as illustrated by Figures S1 and S2. However, when a calculation explicitly including the water electrons is performed, the eigenenergy is raised by  $\delta_1 = \sim 227$  meV. This is a direct result of charge transfer from the water, which decreases the electron's attraction to the  $\text{Na}^+$ , something that is not accounted for with pairwise-additive pseudopotentials.

As we will see in the next section, when a hydrated electron forms a contact pair with  $\text{Na}^+$ , the cation has on average three water molecules in its first solvation shell, but the above calculations are only for a single water. Thus, we also performed a series of calculations to determine the ground-state eigenenergy for an excess electron interacting with  $\text{Na}^+$  that is solvated by one, two, and three water molecules. We held the water molecules equidistant from the cation and oriented perpendicular to one another, so that overlap between multiple solvating waters was negligible. The results of these calculations are summarized in Table 3. We find that although

**Table 3. Electron Binding Energies of  $\text{Na}^+:\text{H}_2\text{O}$  Complexes with a Varying Number of Water Molecules<sup>a</sup>**

no. of waters ( <i>i</i> )	HF,Dipole (eV)	HF,Full (eV)	$\delta_i$ (eV)
0		4.940 50	
1	4.273 28	4.046 33	0.227
2	3.689 86	3.356 25	0.334
3	3.221 01	2.865 90	0.355

<sup>a</sup>The value of  $\delta_i$  is the difference between the binding energies from the  $U_{\text{HF},\text{Dipole}}$  and  $U_{\text{HF},\text{Full}}$  methodologies for  $\text{Na}^+$  solvated by *i* waters. The binding energy of the bare  $\text{Na}^+$  is presented on the first row for reference. The  $\delta_3$  value of 0.355 eV from the bottom row was used to shift the calculated contact pair spectrum in Figure 1B.

charge transfer from the first water leads to a shift of the electron eigenenergy,  $\delta_1 = 227$  meV, the second solvating water only causes an additional 107 meV shift, and the third water yields only another 21 meV shift, indicating that the charge transfer effect saturates quickly with additional waters to  $\delta_3 = 355$  meV.

In the Supporting Information, we argue that although this charge transfer phenomenon also affects the excited states, the energetic shifts of the excited states due to nonpairwise additivity are much smaller than that experienced by the ground state. This is because the excited state appears to bound more by the surrounding water than by  $\text{Na}^+$ , so that the pairwise-additive approximation likely works better for the excited states than the ground state. We are therefore able to estimate the correction to the energy gap and thus the computed spectrum by using  $\delta_3$ , the corrected shift of the ground-state energy.

Of course, the presence of such large shifts in the eigenenergy due to nonpairwise additivity leads directly to the question of whether or not the use of pairwise-additive pseudopotentials in MQC simulations produces meaningful configurations for excess electrons in aqueous electrolytes. Figure 3A shows that in the  $\sim 1$ –2.5 bohr attractive region

where the excess electron sits in the contact pair the pairwise-additive  $U_{\text{Addition}}$  potential and the all-electron  $U_{\text{HF},\text{Full}}$  potentials are essentially parallel: the inclusion of charge transfer between the water and the cation vertically shifts the potential but does not qualitatively affect its shape. This means that the two potentials have similar gradients, so that the forces computed by using the pairwise-additive potential are effectively the same as what they would have been if charge transfer were better accounted for, as shown explicitly in Figure 3B. Thus, the structures and dynamics produced in the MQC simulation should be correct, and the only significant error is an energetic shift ( $\delta_3$ ) that can be included after the fact.

With this understanding of how our MQC simulations overbind the electron to the  $\text{Na}^+$  because charge transfer from water to  $\text{Na}^+$  was not properly accounted for, we can now revisit the calculated spectroscopy of hydrated electrons in the presence of a sodium cation. In the Supporting Information, we show in Figure S3 that the shift of the ground-state eigenenergy due to nonpairwise-additivity mirrors the shift of calculated absorption spectrum. The green solid curve with cross markers in Figure 1 shows that by applying our calculated  $\delta_3 = 355$  meV (for an electron in a contact pair with a multiply solvated  $\text{Na}^+$ ) to shift the simulated absorption spectrum, the simulated and experimental absorption spectra are now in excellent agreement. To get a more quantitative agreement with experiment, one would either need to perform *ab initio* simulations or calculate on-the-fly in MQC trajectories how the shift due to nonpairwise additivity changes in different local configurations, neither of which are computationally feasible and thus beyond the scope of the present work. The fact that calculating a representative average shift gives good agreement with experiment, however, suggests that the simulations are indeed producing the correct underlying physics, allowing us to explore the salt concentration dependence of the hydrated electron's properties in the next section.

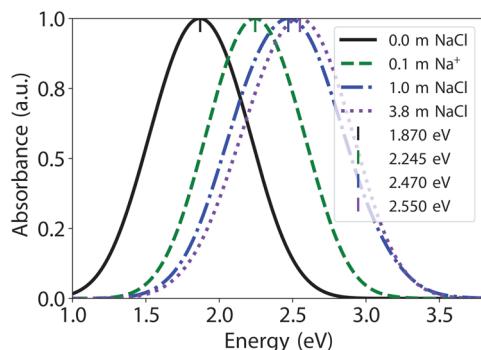
**Salt Concentration Effect on the Structural and Electronic Properties of the Hydrated Electron.** With the cause of the  $(\text{Na}^+, e^-)$  contact pair's exaggerated spectral shift identified and confidence that the MQC simulations are producing the correct structure and dynamics, we now turn to exploring how the hydrated electron's properties depend on salt concentration. Experimentally, the hydrated electron's absorption spectrum undergoes a spectral blue-shift that follows a roughly linear dependence on salt concentration up until NaCl concentrations of  $\sim 2$  *m*, after which the magnitude of the blue-shift begins to saturate.<sup>16</sup> The magnitude of the spectral shift cannot be readily explained by a contact pair involving a single cation<sup>20–22</sup> and is also known to depend on the anion's identity.<sup>16</sup> It is also unclear to what extent the changing dielectric environment of the electrolyte solution is responsible for all or part of the spectral shift as the salt concentration is increased. Thus, in this section we explore the properties of hydrated electrons in aqueous NaCl solutions of 0.1, 1.0, and 3.8 *m* concentration via MQC MD simulation.

To establish a direct connection between our simulations and experiment, we calculated the hydrated electron's absorption spectrum in simulations with different electrolyte concentrations. We computed the oscillator strengths ( $\mu_{0,i}$ ) between the ground state and the three lowest-lying excited states for configurations extracted from the equilibrated trajectories every picosecond and used them to generate absorption spectra in the inhomogeneous limit (eq 1) by sorting the  $\mu_{0,i}$  into 0.01 eV wide bins based on the

corresponding transition energies ( $\Delta E_{0,i}$ ). The generated stick spectra were then convoluted with a Gaussian of  $\sigma = \frac{1}{4\sqrt{2}} \text{ eV}$ .

$$I(E) = \sum_{i=1}^3 |\mu_{0,i}|^2 \Delta E_{0,i} \delta(E - \Delta E_{0,i}) \quad (1)$$

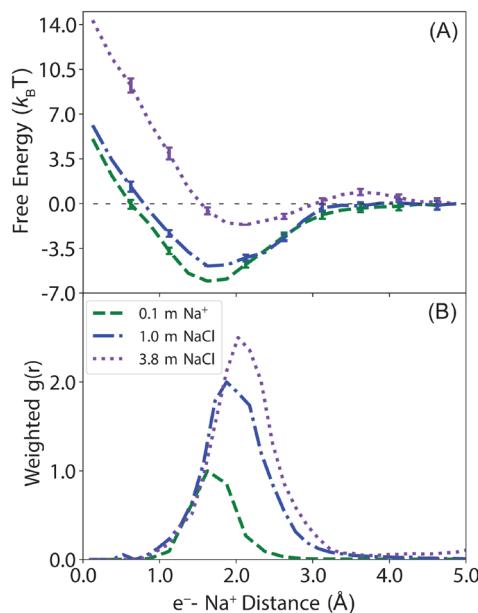
The results are presented in Figure 4, which shows that the simulated spectra indeed behave like experiment: the



**Figure 4.** Normalized absorption spectra of the hydrated electron in NaCl solutions of varying concentration, calculated from MQC simulations. The black solid curve presents the calculated hydrated electron's spectrum in pure water for reference. The green dashed curve shows the spectrum of the  $0.1 \text{ m Na}^+$  system. The simulated spectra of the electron in  $1.0$  and  $3.8 \text{ m NaCl}$  aqueous solutions are plotted with blue dashed and purple dotted curves, respectively. The positions of the spectral maxima use the same color scheme and are listed from top to bottom in order of increasing concentration. The concentration-dependent trend—roughly linear shift at lower concentrations and saturating above  $2.0 \text{ m}$ —matches well with what is observed experimentally.<sup>16</sup>

magnitude of the spectral blue-shift is significant at lower salt concentrations and then largely saturates when the amount of electrolyte reaches higher concentrations. Interestingly, we observe an asymmetrical broadening of the spectrum's shape that is dependent on the salt concentration: the red side of the spectrum is enhanced relative to the blue side at higher salt concentrations. As mentioned above, Mostafavi and co-workers concluded that there was no change in spectral shape with added salt,<sup>16</sup> but Kreitus reported an increase in the half-width of the excess-electron's spectrum in LiCl solutions ranging in concentration from  $0$  to  $15 \text{ M}$ ,<sup>40</sup> so this observation could be consistent with experiment.

Because the simulated spectra show the correct experimental behavior, we turn next to investigate the interactions that underlie the salt concentration-dependent spectral blue-shift of the hydrated electron. Figure 5A shows potentials of mean force (PMFs), computed via the CP-QUS method,<sup>24</sup> for a hydrated electron in the presence of different concentrations of NaCl. The green dashed curve shows the results for a hydrated electron in the presence of a single sodium cation; the electron forms a stable contact pair at an average center of mass to cation distance of  $1.75 \text{ \AA}$ , with a well that is  $\sim 6 k_{\text{B}}T$  deep, as we have discussed previously.<sup>22</sup> The blue dot-dashed curve shows that increasing the concentration of salt by an order of magnitude makes little change: the attractive well in the PMF becomes slightly shallower, likely due to screening of the electrostatic interactions by the presence of additional ions. In addition, the PMF minimum moves to slightly longer



**Figure 5.** (A) Potentials of mean force (PMFs) between the  $\text{Na}^+$  and hydrated electron center of mass in NaCl solutions with different concentrations, calculated by using the CP-QUS method.<sup>24</sup> The green dashed curve shows the PMF in the  $0.1 \text{ m Na}^+$  solution. The PMFs for the  $1.0$  and  $3.8 \text{ m NaCl}$  solutions are plotted as the blue dashed and purple dotted curves, respectively. The shallowness of the  $3.8 \text{ m}$  PMF is likely due to the fact that an unrestrained sodium cation can pair with the hydrated electron as the distance of the restrained sodium cation is increased. (B) Hydrated electron center of mass to  $\text{Na}^+$  pair distribution function,  $g(r)$ , weighted by the average number of cations found within a  $4 \text{ \AA}$  distance. Clearly both the number of  $\text{Na}^+$ 's and their average distance increase with increasing salt concentration.

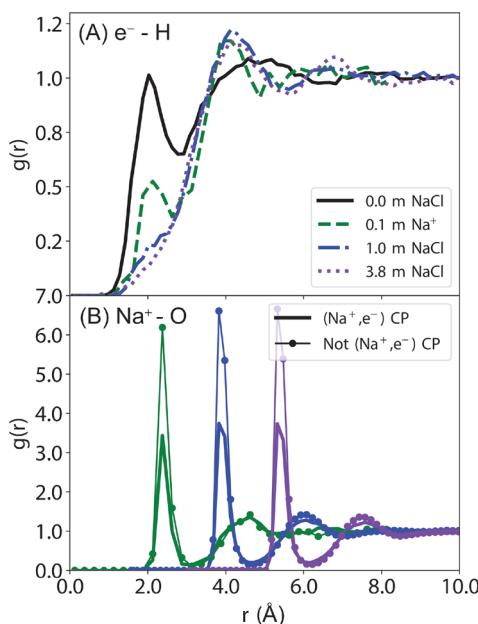
distances, showing that increasing salt concentration does not drive cations closer to the electron's center of mass.

At the highest salt concentration, the violet dotted curve in Figure 5A shows that the free energy attractive well between the hydrated electron and the sodium cations becomes much shallower. However, this change in the cation–electron interaction likely reflects an artifact in the way the PMF is calculated. In calculating the PMF, we restrain only the distance between a single sodium cation and the hydrated electron's center of mass. However, at high salt concentrations, when the “tagged” sodium cation is moved to farther distances from the hydrated electron, another sodium cation that is not restrained can move in to take its place. Thus, the shallow PMF does not necessarily indicate a decreased free energy of interaction between the cations and the hydrated electron at high salt concentrations; rather, it is a hallmark of the fact that it is easy for cations to approach and leave the vicinity of the electron if other cations are nearby enough to take their place.

Figure 5B shows the concentration-dependent arrangement of sodium cations relative to the hydrated electron's center of mass. Clearly, the average distance between the nearest sodium cation(s) and the hydrated electron slightly *increases* with increasing salt concentration. This is consistent with the PMFs in Figure 5A, verifying that the observed concentration-dependent spectral blue-shift is not simply inversely related to the average cation–electron distance.<sup>21,22</sup> The integrated areas under these distributions indicate that the number of sodium cations in the vicinity of the electron changes with NaCl

concentration, a feature we will discuss in more detail further below.

To better understand why the PMFs in Figure 5A have the shape they do, we investigate the local structure of the hydrated electron and electrolyte ions in Figure 6. The



**Figure 6.** (A) Radial distribution function of water H atoms around the hydrated electron center of mass in different solution environments: no electrolyte, black curve; 0.1 m Na<sup>+</sup> solution, green dashed curve; 1.0 and 3.8 m NaCl solutions, blue dashed and purple dotted curves, respectively. The hydrated electron becomes less solvated by water as the salt concentration is increased. Electron–oxygen pair distribution functions are shown in the Supporting Information. (B) Na<sup>+</sup>–water O pair distribution function separated into sodium cations that are part of (Na<sup>+</sup>, e<sup>-</sup>) contact pairs (thick unmarked curves, same color scheme as panel A) and those cations that are more than 4 Å away from the hydrated electron's center of mass (thin curves marked with colored dots). For clarity, the blue 1.0 m and purple 3.8 m curves are shifted to the right by 1.5 and 3.0 Å, respectively. Sodium cations also become less solvated by water if they are participating in a contact pair with the hydrated electron.<sup>22</sup>

unmarked thick solid curves in Figure 6B show radial distribution functions,  $g(r)$ 's, of the water molecules around those sodium cations that lie within 4.0 Å of the hydrated electron's center of mass and thus can be considered to reside in (Na<sup>+</sup>, e<sup>-</sup>) contact pairs; the curves for different salt concentrations are offset horizontally for ease of comparison. For reference, the thin solid curves marked with circles show the same Na<sup>+</sup>–water oxygen  $g(r)$ 's for Na<sup>+</sup> ions that are *not* within 4 Å of the excess electron. The different heights of the first-shell peaks of the marked and unmarked curves make clear that the sodium cations that are in contact pairs with the hydrated electron are less well solvated by water than those in bulk solution.

Figure 6A shows the structure of the water H atoms around the hydrated electron as a function of NaCl concentration (the electron–O atom radial distribution functions are similar but displaced by ~1 Å, as shown in the Supporting Information). As we have discussed in previous work,<sup>22</sup> hydrated electrons that are in contact pairs with sodium cations are more poorly solvated by water H atoms than bulk hydrated electrons, an

effect that clearly gets stronger with increasing salt concentration. Thus, Figures 5 and 6 reflect the delicate balance between cation solvation, electron solvation, and cation–electron overlap that determines the stability of hydrated (Na<sup>+</sup>, e<sup>-</sup>) contact pairs,<sup>22</sup> showing that this balance changes with salt concentration.

When the excess electron forms a contact pair with Na<sup>+</sup>, the electron has direct electronic interactions with both the water and the electrolyte ions. To better understand these interactions and how they affect contact pair stability, we examined the fraction of the excess electron's charge density that is in direct contact with either the surrounding water molecules or the surrounding sodium cations. We refer to this as the direct overlap,  $\Theta$ , given by

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

where the angled brackets indicate an ensemble average,  $\Psi$  is the excess-electron's normalized wave function,  $r_i$  is either the water–electron or cation–electron distance, as desired, and the sum runs over all water molecules or all cations. On the basis of previous work,<sup>11,22,41</sup> we chose the integral's upper limit  $r_c$  to be 1.0 and 2.0 Å for H<sub>2</sub>O and Na<sup>+</sup>, respectively. The results for the contact pairs at the PMF minimum at each concentration are presented in Table 4. As the salt concentration increases, there is more direct contact of the electron's wave function with sodium cations and less direct contact with water.

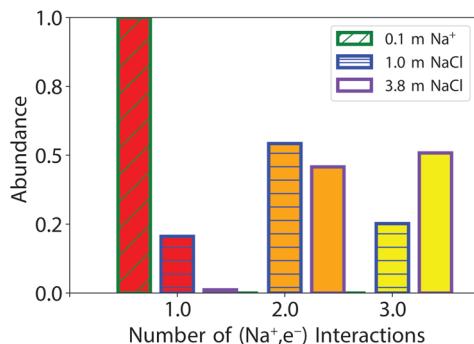
**Table 4. Direct Overlap (Eq 2) of the Hydrated Electron with Sodium Cations and Water Molecules in Different Solution Environments<sup>a</sup>**

	Na <sup>+</sup> direct overlap	H <sub>2</sub> O direct overlap
0.1% m Na <sup>+</sup>	30.35%	2.15%
1.0% m NaCl	29.42%	2.02%
3.8% m NaCl	52.07%	1.89%
hydrated electron (no Na <sup>+</sup> )		5.7%
gas-phase Na atom	53.28%	

<sup>a</sup>As the salt concentration and thus number of cations involved in contact pairs increase, the direct overlap of the electron with the cations increases and the overlap with water decreases.

The data in Table 4 lead to several questions. Why does the degree of Na<sup>+</sup>–e<sup>-</sup> overlap increase with increasing concentration, even though the average distance between the electron and nearby cations increases with increasing concentration (cf. Figure 5)? And more importantly, how can the increasing cation–electron distance with increasing salt concentration be reconciled with increased spectral blue-shift? The answer to both of these questions lies in the fact that the number of sodium cations in proximity to the electron increases with increasing salt concentration. Thus, the total overlap between the electron and Na<sup>+</sup> goes up because the electron overlaps with multiple cations, and attraction to several cations in turn is what is responsible for the increased blue-shift at higher salt concentrations.

The ability for a hydrated electron to form simultaneous contact pairs with multiple Na<sup>+</sup> ions is documented in Figure 7, which shows the relative abundance of contact pairs (defined as a sodium cation residing within 4.0 Å of the electron's center of mass) with different numbers of cations as

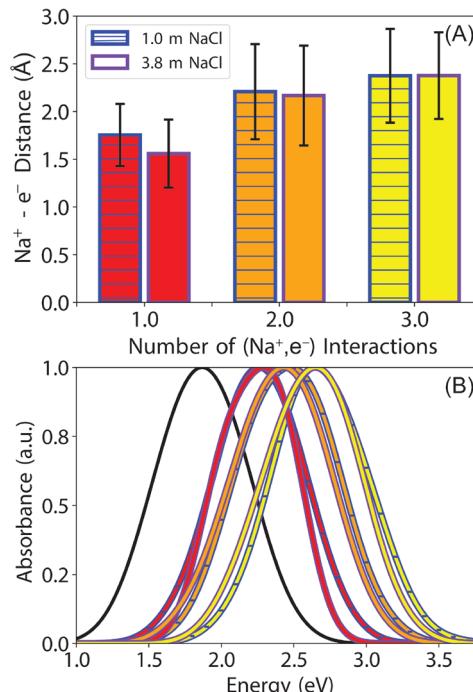


**Figure 7.** Number of sodium cations interacting in  $(\text{Na}^+, \text{e}^-)$  contact pairs (defined as having a distance less than 4 Å from the electron's center of mass) at different salt concentrations. Depending on the salt concentration, contact pairs with 1 (red), 2 (orange), or 3 (yellow)  $\text{Na}^+$  cations are observed. Green, blue, and purple shading denote the  $0.1 \text{ m Na}^+$ ,  $1.0 \text{ m NaCl}$ , and  $3.8 \text{ m NaCl}$  solutions. The number of  $\text{Na}^+$ 's simultaneously paired with the hydrated electron clearly increases with increasing salt concentration, with an average of 1.0 paired  $\text{Na}^+$ 's at  $0.1 \text{ m}$ , 2.05 paired cations at  $1.0 \text{ m}$ , and 2.45 paired ions at  $3.8 \text{ m}$ .

a function of salt concentration. At low concentrations, the electron forms a contact pair with only a single  $\text{Na}^+$  100% of the time (of course, the simulation of this concentration has only a single cation, which forms a stable contact pair). At  $1.0 \text{ m}$  NaCl concentration, about 60% of the contact pairs have two cations, and the remaining electrons reside in contact pairs with 1 or 3 cations about 20% of the time each, for an average of 2.05 paired cations. At  $3.8 \text{ m}$  salt concentration, the contact pairs all have two or three  $\text{Na}^+$ 's associated with the hydrated electron, in about equal amounts, for an average of 2.45 paired cations. A snapshot of one of the multiply contact-paired configurations is shown in the TOC graphic.

The fact that the number of cations involved in  $(\text{Na}^+, \text{e}^-)$  contact pairs changes as a function of salt concentration allows us to learn more about both the average distance between the cations and the electron as well as the origin of the concentration-dependent spectral blue-shift. The presence of multiple cations causes each to be bound less tightly than a single cation, explaining why the average distance increases, as shown in Figure 8A. Moreover, the presence of multiple cations also explains the concentration-dependent spectral blue-shift. Figure 8B shows the absorption spectrum at each salt concentration broken into contributions from contact pairs with different numbers of cations. This analysis shows clearly the more  $\text{Na}^+$  ions that are associated with the hydrated electron, the bluer the corresponding absorption spectrum—a trend that is independent of salt concentration.

Clearly, the attraction of the electron to multiple cations causes an enhanced spectral blue-shift, and the blue-shift is concentration dependent because the number of cations associated with the electron changes with concentration. This shows conclusively that the model proposed by Boutin and co-workers,<sup>21</sup> which assumed that the average cation–electron distance decreased with increasing salt concentration, does not correctly account for the salt concentration dependence of the hydrated electron's spectral shift. Although the cation–electron distance does in fact influence the magnitude of the blue-shift for a solution with a single  $\text{Na}^+$  ion,<sup>22</sup> the role that distance plays in the spectral shift is minor



**Figure 8.** (A) Average cation–electron distance for  $(\text{Na}^+, \text{e}^-)$  contact pairs based on the number of cations interacting with the excess electron, with the same color scheme as in Figure 7. The average distance between the cation and electron center of mass increases with the number of cations involved in the contact pair, independent of the salt concentration. (B) Simulated absorption spectrum sorted based on the number  $\text{Na}^+$  cations involved in the  $(\text{Na}^+, \text{e}^-)$  contact pair at different salt concentrations. The blue and purple shading denotes the  $1.0$  and  $3.8 \text{ m NaCl}$  solutions, respectively. The number of cations involved in the contact pair is clearly the dominant source of the spectral shift, and the concentration of salt (i.e., the cations not involved in contact pairs with the electron) plays effectively no role in the calculated spectroscopy.

compared to the fact that the number of cations in the contact pair changes with concentration.

With all of this information about the way in which multiple cations can influence the hydrated electron's absorption spectrum, we finish by asking how much of the observed spectral blue-shift, if any, results from the change in solvent dielectric constant with changing electrolyte concentration. To answer this question, we manually selected configurations at different salt concentrations that had both an equal number of cations in the contact pair and a roughly equal average  $\text{Na}^+–\text{e}^-$  distance. The results are presented in Table 5 and show that when the contact pairs have the same general structure, the

**Table 5. Calculated Spectral Maximum,  $E_{\max}$ , for Contact Pairs Containing Exactly Two Sodium Cations within 2.2 Å of the Hydrated Electron's Center of Mass at Different NaCl Concentrations<sup>a</sup>**

NaCl molality	$\langle \text{Na}^+–\text{e}^- \text{ distance} \rangle (\text{\AA})$	$E_{\max}$ (eV)
1.0	2.02	2.52
3.8	2.03	2.49

<sup>a</sup>The results show that the absorption spectrum's maximum is independent of the total number of cations in the bulk solution, confirming that the spectral blue-shift does not result from a change in the dielectric environment of the solution.

presence of other ions in solution does not significantly influence the hydrated electron's spectrum. In other words, the number of cations in the  $(\text{Na}^+, \text{e}^-)$  contact pair is what primarily determines the spectral shift, and the presence of other ions farther from the electron has essentially no effect.

## CONCLUSIONS

In summary, we have explored both the physics involved in mixed quantum/classical simulations of hydrated electrons interacting with metal cations and the reasons underlying the experimentally observed spectral shifts of the hydrated electron as a function of salt concentration. We find that although the energetics of the electron– $\text{Na}^+$  interaction are altered between the gas phase and aqueous solution in a nonpairwise-additive fashion, the gas- and solution-phase forces are similar, so that MQC simulations produce reasonable structures and dynamics with an easily accounted-for energetic shift. We also find that the reason the hydrated electron's absorption spectrum blueshifts with increasing salt concentration is because the electron can interact simultaneously with multiple cations, and the number of cations interacting with the electron is concentration-dependent. The cation–electron distance actually slightly increases with added salt, and the surrounding electrolyte solution appears to make little difference in the observed spectroscopy.

All of the results indicate that despite the fact that the hydrated electron can interact simultaneously with up to three sodium cations, the resulting multiple contact pair still behaves electronically more like a slightly perturbed hydrated electron than something more akin to a solvated neutral  $\text{Na}$  atom or  $\text{Na}_2^+$  or  $\text{Na}_3^{2+}$  cation. This observation is in sharp contrast to the behavior observed in liquid tetrahydrofuran, where  $(\text{Na}^+, \text{e}^-)$  contact pairs have electronic properties and spectra that are almost exactly midway between those of a bare solvated electron and a solvated  $\text{Na}$  atom.<sup>42,43</sup> We believe that the difference results in the unique solvation properties of liquid water. Water is so good at solvating ions, even somewhat hydrophobic ions like cavity solvated electrons,<sup>44</sup> that aqueous ions and hydrated electrons prefer to stay solvated relatively independently, despite the favorable electrostatics when they are brought into contact. We showed both above and in previous work<sup>22</sup> that forming aqueous  $(\text{Na}^+, \text{e}^-)$  contact pairs leads to desolvation of both the cation and the electron. Evidently, at high electrolyte concentrations, it is better to make multiple weak cation–electron interactions and maintain the separate water–electron and water–cation interactions than to increase a single cation–electron interaction, even with the screening provided by the high-concentration electrolyte.

Overall, the interactions between solvents, ions and solvated electrons are subtle and complex, and are highly solvent dependent. The fact that experiments show that the observed spectral shift of hydrated electrons in electrolyte solutions depends on the anion identity as well as the cation identity suggests that there are also subtleties involved in competitive ion pairing between cations, anions and electrons, and we will explore this in future work.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcb.2c01501>.

Ion–electron pseudopotentials; classical LJ parameters; pairwise additivity calculations; eigenstates and spectroscopy; contact pair structure; Figures S1–S5; Tables S1–S3 (PDF)

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### Notes

The authors declare no competing financial interest.

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