

Response to Comments on “Does the Hydrated Electron Occupy a Cavity?”

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Turi and Madarász and Jacobson and Herbert argue that the pseudopotential we derived for the hydrated electron contains inaccuracies that make it overly attractive. We show that our potential is derived correctly and argue that the criticisms presented are not relevant when evaluating a pseudopotential’s accuracy for condensed-phase simulation. Neither critique addresses our central result that the experimental properties of the hydrated electron are consistent with a noncavity picture.

In our original paper (1), we derived a pseudopotential for the hydrated electron to represent its condensed-phase behavior. In their critiques, Turi and Madarász (2) and Jacobson and Herbert (3) argue that our pseudopotential contains inaccuracies that make it overly attractive, such that the noncavity nature of the hydrated electron we reported is unphysical. Here, we note that the derivation of our potential is correct. We also argue that the criteria by which Turi and Madarász and Jacobson and Herbert criticize our potential, which are based on the vertical electron binding energy (VEBE) of an excess electron interacting with either a single water molecule or small clusters, are not relevant for evaluating the quality of a pseudopotential for condensed-phase simulation. Finally, we point out that neither comment addresses the central claim of our paper, which is that our results demonstrate that the known experimental properties of the hydrated electron are consistent with a noncavity picture.

To derive our pseudopotential, we started with a Hartree-Fock (HF) calculation on a single water molecule and determined the lowest unoccupied molecular orbital (LUMO). We then used this LUMO to calculate the Phillips-Kleinman (PK) pseudo-orbital, a wave function that is constructed to be nodeless, to match the LUMO outside the water core molecular orbitals, and to have the same eigenenergy as the LUMO (4, 5). Our pseudopotential was then rigorously determined as that whose one-electron Schrödinger equation has the PK pseudo-orbital as its ground state (4).

When all of the electrons are confined by an external potential, however, the LUMO one obtains is different from that of an unconfined system, so the resulting pseudopotential is also different. Thus, it is not strictly correct for Turi and Madarász (2) to compare their pseudo-orbital, which was calculated using a LUMO with a confining potential, to that generated from our potential, which was based on the unconfined LUMO. Nevertheless, as shown in figure 1A of their comment [and also figure 2A in

(6)], whether or not there is a confining potential, the water pseudo-orbital has features with high electron density near the oxygen atom, which create attractive regions in the PK pseudopotential that reproduces this density. Moreover, to use our pseudopotential in condensed-phase calculations, we smoothed our pseudo-orbital at the resolution of the grid basis set used in our MD simulations (1). Thus, much of the apparent discrepancy in figure 1A of Turi and Madarász (2) results from their choice to compare the raw, unsmoothed PK pseudo-orbital to that reproduced by our potential based on a smoothed pseudo-orbital.

Once we produced our numerically exact, smoothed pseudopotential, we followed the standard approach of fitting it to an analytic function. We could have constrained our fit to guarantee that the resulting analytic potential generated the original eigenenergy, even if this caused the fit to miss some of the physical features of the potential, as has been done by others (6, 7). Instead, we chose a function that best represented the physical features of the potential (1), even though this had the numerical consequence of slightly altering the single-molecule eigenenergy. We took this approach because we felt that it was important to account for the large attractive and (off-atom) repulsive features that have not been included in previous water-electron pseudopotentials. Thus, Turi and

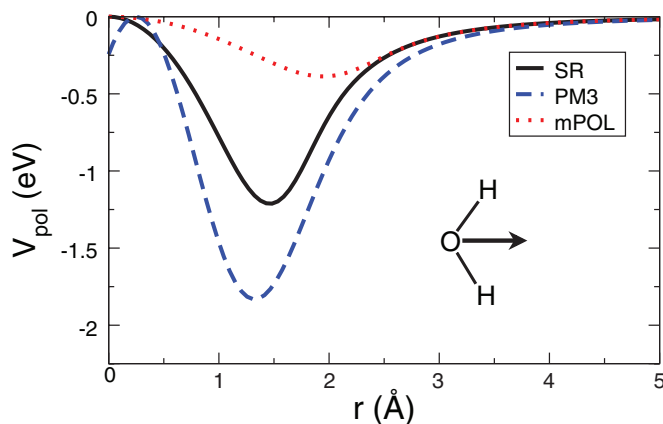
Madarász are correct in pointing out that our choice produces a ground-state eigenenergy for a single water molecule that is slightly overbound.

Despite this slight overbinding, figure 1 of our original paper (1) shows that our fit reproduces the features of the exact PK pseudopotential. Even though Turi and Madarász label the oscillations in our fitted potential ~ 4 Å away from the O atom as unphysical artifacts, these features are present in the exact numerical PK pseudopotential. Smoothing does shift the positions and amplitudes of these features slightly, but their presence likely has no effect in condensed-phase calculations, since an electron ~ 4 Å away from one water molecule in liquid water is certain to be much closer to, and hence interact more strongly with, the nearby water molecules.

Although the PK procedure generates a well-defined single-molecule pseudopotential, the properties of isolated gas-phase water molecules are not the same as those in bulk water (e.g., the dipole moment of a gas-phase water molecule is ~ 1.8 D, whereas in liquid water it is ~ 2.4 D), because interacting water molecules strongly polarize each other. We chose to incorporate the effects of this many-body polarization in two ways: We altered the point charges in our PK-based potential to match those of the classical water molecules (8, 9) used in our condensed-phase simulations, and we also grafted on a pairwise-additive polarization potential originally parameterized by Schnitker and Rossky (SR) (10). Although the SR polarization potential is ad hoc, Fig. 1 shows that it is remarkably similar to the more rigorously derived PM3 polarization potential (11). Thus, we expect our potential (1) to be physically reasonable within the non-inconsiderable constraints of a non-self-consistently determined polarization term, the assumption of pairwise additivity, the necessity of fitting to an analytic function, and the use of a classical water model parameterized for the bulk liquid.

Given how we developed our potential, we believe that Jacobson and Herbert’s (3) claims of supposed errors in our development reflect a

Fig. 1. Comparison of electron-water pairwise-additive polarization potentials. The SR (10) polarization potential (black curve) used in our study is quite similar to Sommerfeld *et al.*’s (11) PM3 polarization potential (blue dashed curve), which corresponds to a Born-Oppenheimer limit of their Drude-oscillator configuration interaction model. For comparison, the modified polarization potential used by Jacobson and Herbert (3) (mPol) is shown as the red dotted curve. The mPol potential clearly underbinds electrons relative to the other polarization potentials that were designed for use in either cluster (PM3) or condensed-phase (SR) environments. The potentials are plotted as functions of distance, r , from the oxygen atom along the water dipole, as indicated by the inset.



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fundamental misunderstanding of pseudopotential theory. First, Jacobson and Herbert claim that our potential is overly attractive near the hydrogen atoms because the density of the water PK pseudo-orbital has a maximum in this region, whereas the density of the exact static-exchange wave function (HF LUMO) is at a minimum. However, this difference arises because the HF water LUMO has a node close to the H atoms, whereas the PK pseudo-orbital is nodeless by construction (4, 5). PK pseudopotentials are based on pseudo-orbitals, not LUMOs (4), and because the exact PK water pseudo-orbital has a density maximum near the H atoms [see, for example, figures 1 and 2 in (6)], this requires a minimum in the PK pseudopotential that reproduces this density. Second, Jacobson and Herbert note that our potential gives a different behavior from HF theory, from which it was derived. This is not surprising: As pointed out above, we modified the point charges in our PK potential and added the SR polarization term to account for (in a pairwise-additive way) the correlation/dispersion interactions that are missing in HF theory (11). Thus, optimizing a water cluster anion with HF theory and with our potential should lead to different structures with different wave functions.

Even though our potential was designed for the condensed phase, Jacobson and Herbert assert that cluster VEBEs are an appropriate benchmark for testing our potential. In their figure 1 (3), they compare VEBEs determined with our potential to MP2 calculations and conclude that our potential overbinds the electron in water anion clusters. Although we never expected our potential to provide an accurate means to replace high-level quantum chemistry calculations for water anion clusters, in

Table 1. VEBEs, in meV, of water cluster anions from ab initio calculations at the CCSD(T) level (11), our pseudopotential (LGS) (1), and the modification of the polarization term in our pseudopotential (LGS-mPol) proposed by Jacobson and Herbert (3); the number in parentheses shows the difference between the pairwise-additive and ab initio results. The mean differences from the ab initio results are for our LGS potential +40 meV (all clusters) and +38 meV (only $n = 6$ clusters), whereas those for Jacobson and Herbert's LGS-mPol potential are -165 meV (all clusters) and -197 meV (only $n = 6$ clusters).

Cluster*	Ab initio†	LGS (diff)‡	LGS-mPol (diff)‡
W2 (S)	41	93 (+52)	67 (+26)
W6A (S)	470	537 (+67)	284 (-186)
W6B (S)	610	528 (-82)	309 (-299)
W6C (S)	340	580 (+240)	279 (-61)
W6D (S)	380	339 (-41)	217 (-163)
W6E (I)	550	527 (-23)	322 (-228)
W6F (I)	780	847 (+67)	536 (-244)

*Cluster geometries are taken from (11). The number indicates the cluster size, the letter indicates which isomer, and the letter in parentheses denotes whether the electron is bound to the surface (S) or in the interior (I) of the cluster. †Calculated at the CCSD(T) level, taken from (11). ‡Calculated using identical grid parameters to the bulk e_{aq}^- simulations of (1).

Table 1 we show the energies of several small water anion clusters computed with both our potential and high-level coupled-cluster singles and doubles with perturbative triples [CCSD(T)] calculations (11). For all but one cluster (W6C), our potential reproduces the VEBEs remarkably well, a clear indication that it works in cases beyond that for which it was originally designed. It is worth noting that Jacobson and colleagues themselves have developed a (non-pairwise-additive) electron-water pseudopotential that accurately reproduces the VEBEs of water anion clusters (7); when they transferred this potential to the bulk, however, they got a noncavity electron, and this potential had to be substantially redesigned to remove the noncavity behavior (12).

We agree with Jacobson and Herbert that the apparent ~2 eV overbinding of the bulk electron with our potential could be of concern. However, given that condensed-phase VEBEs are sensitive to long-range interactions (13), we expect that one could make up the ~2 eV without inducing cavity formation by replacing our ad hoc polarization term with a many-body self-consistent polarization model [as was done by Herbert and Jacobson (12) to get a noncavity electron], so that the longer-range portion of the effective electron-water interaction would be weaker. This also would likely correct any discrepancy with the VEBEs of the larger clusters in Jacobson and Herbert's figure 1 (3).

Interestingly, both Turi and Madarász (2) and Jacobson and Herbert (3) propose modifications of our potential to correct for what they see as overbinding. In Turi and Madarász's case, our potential was adjusted to no longer have the correct physical form but to guarantee the correct single-molecule eigenenergy; in Jacobson and Herbert's case, the SR polarization term was effectively shut off (Fig. 1), leaving only the gas-phase PK pseudopotential, which underbinds the electron to small clusters (Table 1) but does better for larger clusters. What these modifications show is that potentials that are parameterized to match VEBEs for single molecules or small clusters can give extremely different behavior in the bulk. In fact, the potential in (6) is constrained to give the exact same single-molecule eigenenergy as that in figure 1B in (2), but these two potentials (which use distinct ad hoc polarization models) predict strikingly different bulk hydrated electrons. For example, Turi and Madarász's modification of our potential gives more than ten water molecules in the electron's first solvation shell, versus only four with the potential in (6).

What both of the critiques show is that fitting VEBEs does not constrain the universe of pseudopotentials sufficiently to define a unique pairwise-additive pseudopotential for use in the condensed phase. Neither Jacobson and Herbert (3) nor Turi and Madarász (2) make a case for why their chosen VEBE-based measure provides the best criterion by which to judge a potential, and there is no acknowledged "best" procedure in the literature for transferring single-molecule PK potentials for

use in condensed phases. We believe that when extending single-molecule potentials for use in condensed-phase calculations, it is most important to get the overall shape of the potential right if pairwise additivity is to have any hope of success. Thus, we contend that Turi and Madarász and Jacobson and Herbert's criticisms reflect these authors' biases about how to construct "good" potentials; their arguments provide grounds for legitimate scientific discourse, but they do not provide proof that any particular potential is the best for use in the bulk case.

In our original paper (1), we argued that the best way to test a potential for use in the bulk is to compare its predictions to condensed-phase experimental measurements. With the exception of the bulk VEBE discussed above, our hydrated electron simulations agree with the experimental absorption spectrum, polarized and unpolarized absorption transients, and diffusion constant. Jacobson and Herbert (3) claim that our potential gives a diffusion constant that is too large, but our simulations give $D = 2.0 \pm 0.6 \times 10^{-5}$ cm²/s (error bars are $\pm 2\sigma$), a factor of ~2 smaller than experiment (14) but similar to that given by most cavity models (15). Given that our simulations match so many experimental results as well or better than cavity-based models, we remain unconvinced that the VEBE criterion is all-important when determining the effectiveness of a potential for use in the condensed phase.

Turi and Madarász (2) have also pointed out that our results appear to contradict recent ab initio simulations (16), which show excess electrons in water occupying a cavity. Thus far, though, the simulations have been performed only for small numbers of water molecules in clusters. With our potential, we found substantial finite-size effects, such that even with 200 water molecules there were large fluctuations that did not occur with 500 waters (1). This sensitivity to system size could be indicative of the importance of long-range forces in establishing the solvation environment of the hydrated electron. Pending extension to larger system sizes and the further vetting of new density functionals (12, 17), we believe it is best to withhold judgment while noting our great interest in these ab initio results.

The current debate brings us to the question of precisely what is the proper balance between attraction and repulsion for electron-water interactions. It is well known (18) that for potentials dominated by repulsion, temperature changes have little effect on liquid/solute properties if the density is kept constant. In contrast, when attractive forces play a substantial role, changing the temperature at constant density alters solute properties. Experiments have shown that the absorption spectrum of the hydrated electron does shift with temperature at constant density (19), a result that is not reproduced by simulations based on a cavity model (20). Thus, we speculate that even if our potential proves to be somewhat too attractive, it will turn out that the balance between attraction

and repulsion also has not been properly accounted for in previous potentials.

We close by reiterating that although it was derived using a rigorous procedure, even if our potential were entirely ad hoc, it constitutes an existence proof that the known experimental properties of the hydrated electron are consistent with a noncavity picture. In addition to the discussion comparing properties of the noncavity electron to experiment in our paper (*I*), it is known experimentally that the molar solvation volume of the hydrated electron is negative (*2I*). This feature is consistent with the enhanced water density we see inside the noncavity electron with our potential (*I*) and is harder to rationalize with cavity-based models. Ultimately, as noted in our study, it will be up to future experiments and calculations to determine whether or not the hydrated electron resides in a cavity.

References and Notes

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