Comment on "Does the Hydrated Electron Occupy a Cavity?"

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Larsen *et al.* (Reports, 2 July 2010, p. 65) suggest that, contrary to the established paradigm, the aqueous electron does not carve out and occupy a cavity in liquid water. Closer examination of their theoretical model, however, reveals that many of its predictions differ substantively from established benchmarks and that its behavior differs qualitatively from Hartree-Fock theory, upon which the model is based.

A recent report by Larsen, Glover, and Schwartz (*1*) (LGS) challenged the long-held view that the "hydrated" (aqueous) electron, e^-_{aq}, consists of a one-electron wave function localized within a quasispherical solvent cavity and coordinated to four to six water molecules. This has been the dominant paradigm for more than 40 years (*2*), and it is supported by numerous atomistic simulations (*3*–*5*). The challenge by LGS is based on a new, "rigorously derived" electron-water pseudopotential, and simulations using this one-electron pseudopotential model do not afford a well-defined cavity. This model, however, has not yet been tested against reliable benchmarks. Such tests are reported here.

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The LGS pseudopotential (*1*) is derived within the static exchange (SE) approximation, which essentially amounts to a Hartree-Fock calculation for H_2O^- using frozen molecular orbitals (MOs) for H_2O. LGS have devised a clever way to obtain a nodeless pseudo-orbital for the unpaired electron without introducing approximations that are typically made in this context (*6*). Once the pseudo-orbital is determined, it can be converted into an electron-water pseudopotential for condensed-phase simulations.

The LGS pseudopotential was fit using Mulliken atomic charges $Q_O = -0.862709e$ and $Q_H = +0.431355e$ obtained from a Hartree-Fock calculation, but e^-_{aq} simulations were performed using $Q_O = -0.82e$ and $Q_H = +0.41e$, corresponding to the simple point charge (SPC) water model (*1*). This corresponds to a reduction in H_2O dipole moment from 2.39 D to 2.27 D, at the SPC geometry. LGS augmented their model with an approximate polarization potential, which is not included in the SE treatment, and far less attention is paid to this aspect of the model. Polarization parameters from the literature were used, without further comment.

High-level ab initio calculations have been reported for $(H_2O)^-_n$ clusters, for $n = 2$ to 33 (*7*), but LGS did not report any comparisons to these data. Figure 1A compares benchmark ab initio vertical electron binding energies (VEBEs) to results obtained using the LGS pseudopotential. The LGS model strongly overbinds the electron compared with ab initio calculations. By modifying a single parameter in the polarization potential (R_c) [see supporting online material for (*1*)], we obtain a model that we call LGS-mPol that performs reasonably well against this benchmark database, albeit not as well as other hydrated-electron models in the literature (*4*, *5*, *7*). We do not intend LGS-mPol to be a serious e^-_{aq} model, but rather to demonstrate that the overbinding exhibited by the LGS model cannot be fixed in a simple way, without deleterious effects on other observable properties.

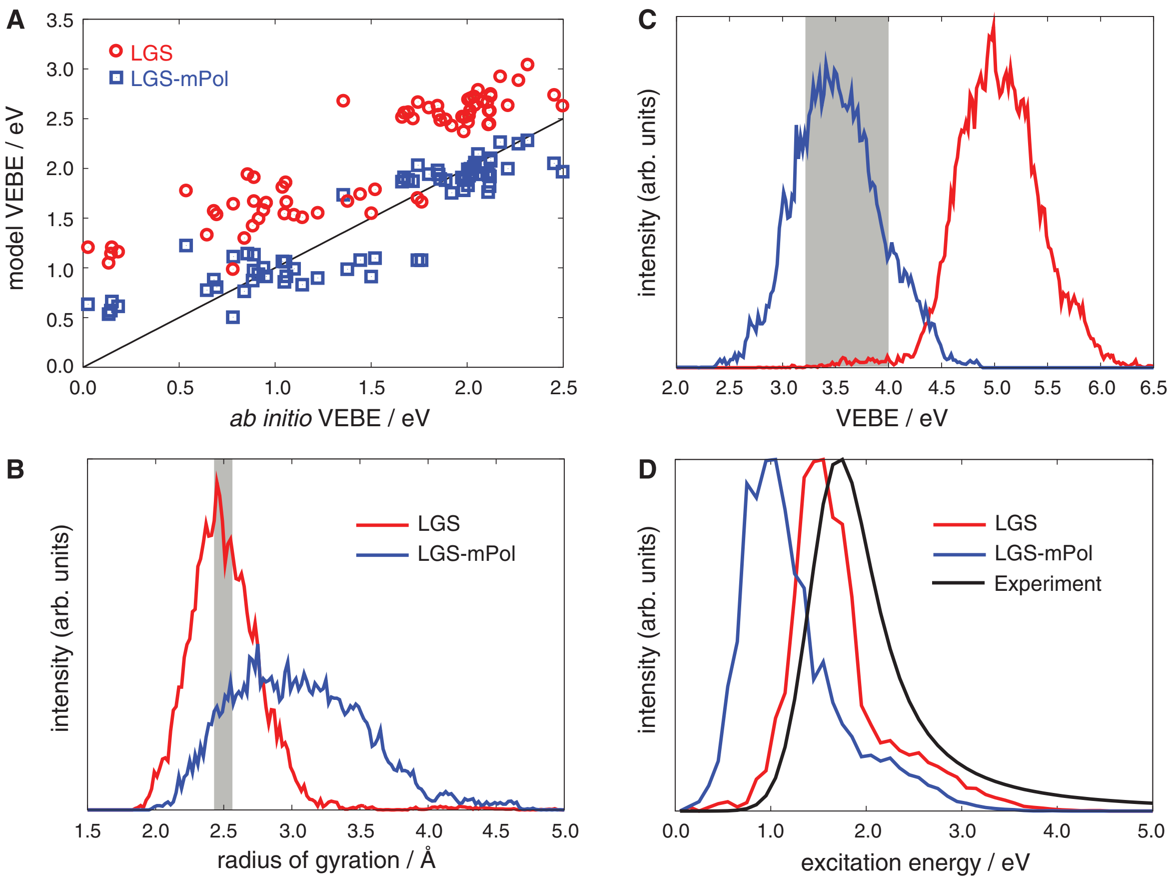
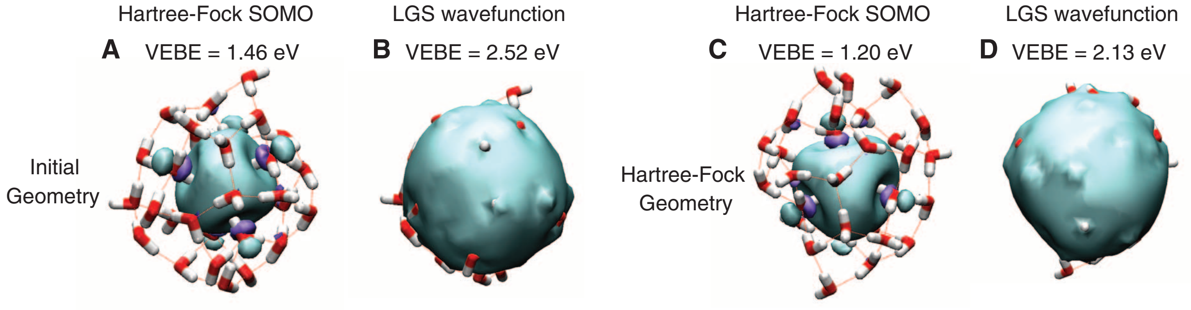


Fig. 1. (**A**) Comparison of MP2/6-31(1+,3+)G* benchmark VEBEs (*7*) to results obtained using LGS-based pseudopotential models, for 71 different $(H_2O)^-_n$ isomers ranging from n = 12 to n = 33. (**B** to **D**) Radius of gyration, VEBE, and optical absorption spectrum of e^-_{aq}, obtained from bulk simulations. The gray boxes in (B) and (C) depict the range of the experimental estimates of these quantities (*8*–*12*).



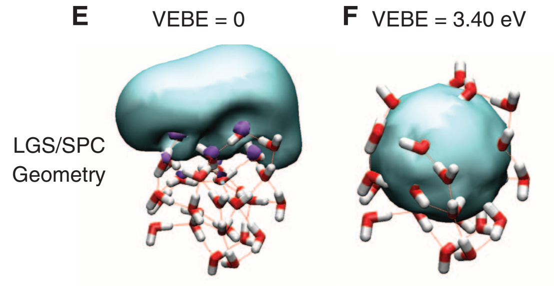


Fig. 2. Results of optimizing a cavity-bound $(H_2O)^-_{31}$ structure. The initial geometry (**A** and **B**) was carved out of a bulk e^-_{aq} simulation and clearly exhibits a compact, cavity-bound wave function at the HF level. The cluster geometry in (**C**) and (**D**) is the HF minimum-energy geometry, although the wave function in (D) is calculated using the LGS model. The cluster geometry in (**E**) and (**F**) is the LGS minimum-energy geometry, although the wave function in (E) is the HF SOMO. Each isosurface encapsulates 0.9*e*.

We have performed molecular dynamics simulations of e^-_{aq} using the same simulation procedure reported in (*1*). We find that radial distribution functions and other structural properties reported by LGS are not strongly affected by variation of the polarization potential or the H_2O point charges. Rather, it is the LGS pseudopotential itself that is indisposed toward cavity formation.

Figure 1, B to D, shows several properties obtained from our simulations and compares them to experimental estimates. The average radius of gyration for the LGS model is in good agreement with experiment (*8*), but the agreement is far less satisfactory for the LGS-mPol variant examined here, which performs much better for VEBEs. The optical absorption spectrum predicted by the LGS model is slightly red-shifted, relative to experiment, and a more rigorous treatment of solvent polarization should further red-shift the spectrum (*5*). The attenuated polarization potential in LGS-mPol yields a spectrum that is red-shifted from experiment by 0.7 eV, which makes sense given the larger radius of gyration predicted by this model.

Strikingly, all 29 excited states that we used to generate absorption spectra are vertically bound. In fact, the 29th excited state is bound, in the LGS model, by ~1.0 eV. Figure 1C plots the distribution of ground-state VEBEs obtained from the simulations. The LGS model overbinds the electron by 1 to 2 eV, whereas LGS-mPol predicts a VEBE within the range of experimental estimates for e^-_{aq} (*8*–*12*). This agreement is partly fortuitous, as the binding energy increases by ~1 eV if Ewald summation is used to sum the long-range Coulomb interactions (*5*), whereas we followed the procedure of LGS (*1*) and used the minimum-image convention.

Larsen *et al.* (*1*) plotted the ground-state e^-_{aq} energy as a function of time. This function oscillates around −5.5 eV, whereas the lowest few excited-state energies oscillate between −3 eV and −4 eV. In contrast, the ground-state energy inferred from experiment is 3.4 to 4.0 eV (*8*–*12*). In view of this tremendous discrepancy, the assertion by LGS that "in every case…our predictions are consistent with experiment" appears to be overstated.

Ab initio calculations on $(H_2O)_n^-$ clusters find that orbital relaxation upon electron detachment is fairly minor (*13*); hence, the Hartree-Fock (HF) singly occupied MO (SOMO) should offer a qualitatively correct description of the unpaired electron, provided that this orbital is bound. The LGS pseudopotential, in conjunction with an ad hoc polarization potential, is intended to mimic the HF SOMO. To examine the extent to which it does so, we carved out a $(H_2O)^-_{31}$ cluster from a cavity-forming model of e^-_{aq} (*4*), which represents a 5.5 Å radius around the centroid of the cavity-bound wave function. The geometry of this cluster was subsequently optimized using HF/6-31++G* theory and, alternatively, the LGS model. Figure 2 shows that HF optimization preserves the cavity-bound nature of the SOMO, but this cavity collapses when optimized using the LGS model. The latter affords a wave function that permeates throughout the cluster. At the LGS-optimized geometry, the HF SOMO is unbound and is localized on the surface of the cluster; it has been "squeezed out" by the collapse of the cavity.

Collapse of the solvent cavity arises because the LGS pseudopotential is far more attractive near the hydrogen atoms than previous pseudopotentials. This feature results from the fact that the density associated with the "exact" pseudo-orbital obtains a maximum over the hydrogen atoms, whereas the density of the exact SE wave function is at a minimum [see figure 1 in (*14*)]. Any pseudopotential derived from this pseudo-orbital will result in a far-too-attractive region near the hydrogen atoms. In contrast to the LGS potential, the true HF potential is clearly repulsive in these regions, as evidenced by the "dents" in the HF SOMO around each water molecule (see Fig. 2).

The structure of e^-_{aq} is intimately quantum-mechanical, and cannot be probed directly by experiment, so there is an acute need for theoretical models to aid in the interpretation of experimental observables. Before new theoretical predictions can be taken seriously, however, such models must be carefully tested against the large body of existing e^-_{aq} data. Relative to the current generation of cavity-forming pseudopotential models (*4*, *5*), the model introduced by Larsen *et al.* (*1*) fares poorly in such tests.

References and Notes

1. R. E. Larsen, W. J. Glover, B. J. Schwartz, *Science* **329**, 65 (2010).
2. E. J. Hart, M. Anbar, *The Hydrated Electron* (Wiley, New York, 1970).
3. J. Schnitker, P. J. Rossky, *J. Chem. Phys.* **86**, 3471 (1987).
4. L. Turi, D. Borgis, *J. Chem. Phys.* **117**, 6186 (2002).
5. L. D. Jacobson, J. M. Herbert, *J. Chem. Phys.* **133**, 154506 (2010).
6. C. J. Smallwood, R. E. Larsen, W. J. Glover, B. J. Schwartz, *J. Chem. Phys.* **125**, 074102 (2006).
7. L. D. Jacobson, C. F. Williams, J. M. Herbert, *J. Chem. Phys.* **130**, 124115 (2009).
8. J. V. Coe, S. M. Williams, K. H. Bowen, *Int. Rev. Phys. Chem.* **27**, 27 (2008).
9. L. Ma, K. Majer, F. Chirot, B. von Issendorff, *J. Chem. Phys.* **131**, 144303 (2009).
10. Y. Tang *et al.*, *Phys. Chem. Chem. Phys.* **12**, 3653 (2010).
11. K. R. Siefermann *et al.*, *Nat. Chem.* **2**, 274 (2010).
12. A. T. Shreve, T. A. Yen, D. M. Neumark, *Chem. Phys. Lett.* **493**, 216 (2010).
13. J. M. Herbert, M. Head-Gordon, *Phys. Chem. Chem. Phys.* **8**, 68 (2006).
14. L. Turi, M.-P. Gaigeot, N. Levy, D. Borgis, *J. Chem. Phys.* **114**, 7805 (2001).
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