

Response to “Comment on ‘An electron-water pseudopotential for condensed phase simulation’ ” [J. Chem. Phys. **131**, 037101 (2009)]

Jurgen Schnitker¹ and Peter J. Rossky^{2,a)}

¹Wavefunction, Inc., 18401 Von Karman #370, Irvine, California 92612, USA

²Department of Chemistry and Biochemistry and Institute for Computational Engineering and Sciences, University of Texas at Austin, Austin, Texas 78712, USA

(Received 15 June 2009; accepted 20 June 2009; published online 15 July 2009)

[DOI: [10.1063/1.3175802](https://doi.org/10.1063/1.3175802)]

We are grateful for the detailed re-examination of Larsen *et al.*¹ of the electron-water pseudopotential that we proposed more than 20 years ago.² The potential was among the first of a number of potentials that were used by various groups in studies of the structure, dynamics, and spectroscopy of solvated electrons.^{3–7} While our potential was based on a more detailed analysis than had been carried out in previous work, it nevertheless included many assumptions and strong approximations. Effectively, it was an *ad hoc* model potential—irrespective of its construction from basic physical arguments. It has been validated, at least on a qualitative level, by comparison to experiment in a number of contexts, most importantly excited state dynamics.^{8–10}

When devising the potential, we considered four fundamental contributions: (i) static Coulomb interactions between the excess electron and the dipolar water molecules, (ii) electrostatic polarization effects, (iii) Pauli repulsion reflecting the orthogonality constraint between the excess electronic wave function and the solvent wave functions, and (iv) exchange interactions. The last were omitted from the final potential, but the other three terms were deemed significant enough to be included.

As Larsen *et al.* showed, an error was apparently made in the calculation of the parameters that are associated with one of the three terms that are represented in the potential.¹ This means that our model potential does not, in fact, follow from the procedure as originally described. Effectively, a correct calculation following the route originally proposed shifts the balance in favor of the repulsive orthogonality term, correspondingly de-emphasizing the Coulomb interaction with the polar water molecules.

However, what Larsen *et al.* observed when simulations are carried out with the “corrected” potential is remarkable.¹ Despite the considerable change in water distribution at a short distance from the electron, *once again* a cavity-like state for the hydrated electron is found—just as has been seen in numerous other studies of hydrated electrons that employed alternative potential functions.^{2–6} There are some differences, in that the relatively smaller contribution of the

polar interaction term leads to a solvation structure¹ that is considerably less akin to that of an anion than was observed in the original simulations.⁴ (One would then conclude that not only anions but also small nonpolar solutes can provide a meaningful reference point for the description of the hydrated electron.) The calculated absorption spectrum is found to be redshifted, albeit without any real change in the lineshape or the underlying origin of that lineshape.

While the spatial details of the hydration structure of hydrated electrons remain unsettled, we believe that the comparison of Larsen *et al.* of the two potential functions only confirms the general robustness of our understanding that has emerged over the past two decades: There is a cavity with an electronic ground state that can be *s*-like, and the main band of the absorption spectrum can be explained by transitions to three excited states that can be *p*-like and that are only approximately degenerate.¹¹ Simulations of hydrated electrons with sophisticated many-electron methods indicate that the precise description of the hydrated electron may be more involved,¹² but the simple cavity model nevertheless continues to serve as a most useful reference point.

^{a)}Electronic mail: rossky@mail.utexas.edu.

¹R. E. Larsen, W. J. Glover, and B. J. Schwartz, *J. Chem. Phys.* **131**, 037101 (2009).

²J. Schnitker and P. J. Rossky, *J. Chem. Phys.* **86**, 3462 (1987).

³M. Sprik and M. L. Klein, *Comput. Phys. Rep.* **7**, 147 (1988).

⁴R. N. Barnett, U. Landman, C. L. Cleveland, and J. Jortner, *J. Chem. Phys.* **88**, 4421 (1988).

⁵C. D. Jonah, C. Romero, and A. Rahman, *Chem. Phys. Lett.* **123**, 209 (1986); C. Romero and C. D. Jonah, *J. Chem. Phys.* **90**, 1877 (1989).

⁶L. Turi and D. Borgis, *J. Chem. Phys.* **117**, 6186 (2002).

⁷L. D. Jacobson, C. F. Williams, and J. M. Herbert, *J. Chem. Phys.* **130**, 124115 (2009).

⁸B. J. Schwartz and P. J. Rossky, *J. Chem. Phys.* **101**, 6917 (1994).

⁹C.-R. Wang, T. Luo, and Q.-B. Lu, *Phys. Chem. Chem. Phys.* **10**, 4463 (2008) and references therein.

¹⁰M. J. Tauber and R. A. Mathies, *J. Phys. Chem. A* **105**, 10952 (2001); *J. Am. Chem. Soc.* **125**, 1394 (2003).

¹¹J. Schnitker, K. Motakabbir, P. J. Rossky, and R. A. Friesner, *Phys. Rev. Lett.* **60**, 456 (1988).

¹²M. Boero, M. Parrinello, K. Terakura, T. Ikeshoji, and C. C. Liew, *Phys. Rev. Lett.* **90**, 226403 (2003).