Comment on "An electron-water pseudopotential for condensed phase simulation" [J. Chem. Phys. 86, 3462 (1987)]

Ross E. Larsen, William J. Glover, and Benjamin J. Schwartz[a)]
Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90095-1569, USA

Some time ago, Schnitker and Rossky derived a pseudopotential describing the interaction of an excess electron with water and used it to study the properties of the hydrated electron with molecular dynamics simulation.[1] The derivation was based on ideas from electron-molecule scattering theory, with the wave function of the water-plus-electron system treated at the single-determinant (Hartree–Fock) level. Schnitker and Rossky's application of this approach to water used the assumption that the pseudo-orbital associated with the pseudopotential is constant across each occupied molecular orbital of the water molecule, and this assumption leads to a particularly simple analytic form for the pseudopotential, which is given by Eq. (3), below.

Many properties of the hydrated electron have been understood in the context provided by the Schnitker and Rossky (SR) pseudopotential, although similar results have been seen with other pseudopotentials.[2] With the published SR pseudopotential, the hydrated electron occupies a nearly spherical cavity and has a radius of gyration of ~2.1 Å. There are six water molecules in the first solvation shell, arranged quasioctahedrally in the so-called Kevan structure,[4] with one hydrogen atom on each first-shell water pointing directly toward the hydrated electron's center of mass [see, e.g., Fig. 2(b)].

Recently, however, we discovered an error in the electron-water pseudopotential published by SR that dramatically changes the predicted properties of the hydrated electron. Thus, we believe it is worthwhile to comment on the nature of the error and to describe how the properties of the hydrated electron change when this error is corrected.

Briefly, the error in the original paper is as follows: with the approximations made by SR, the part of the pseudopotential that accounts for the repulsion of the excess electron by the electrons in the occupied water molecular orbitals takes the form

$$V_R(\mathbf{r}) = -\sum_\alpha \epsilon_\alpha K_\alpha \sum_j c_j^\alpha \chi_j(\mathbf{r}), \tag{1}$$

where α denotes the (occupied) water molecular orbitals, ϵ_α is the energy of orbital α, c_j^α is the coefficient giving the contribution of basis function χ_j to this orbital, and

$$K_\alpha = \sum_j c_j^\alpha \int \chi_j(\mathbf{r}) d\mathbf{r}. \tag{2}$$

According to Eq. (2), only spherically symmetric Slater-type basis functions contribute to K_α, so the integrals reduce to $4\pi \int_0^\infty r^2 \chi_j(r) dr$ for these spherical basis functions. The repulsive part of the pseudopotential thus may be written as a sum over all of the s orbitals in the double-ζ Slater-type basis set used by Schnitker and Rossky, resulting in the form

$$V_R(\mathbf{r}) = \sum_i \sum_{j_i} B_j r^{n_j} e^{-\rho_j r}, \tag{3}$$

where i runs over atomic sites, j_i runs over the spherical basis functions for atomic site i, and

$$B_j = -N_j \sum_\alpha \epsilon_\alpha K_\alpha c_j^\alpha, \tag{4}$$

where N_j is the normalization factor associated with Slater-type orbital j.

We found that the tabulated values of B_j published in Ref. 1 are not consistent with evaluating the integrals needed for K_α as $4\pi \int_0^\infty r^2 \chi_j(r) dr$. We were able to reproduce the values given by SR when the integrals in Eq. (2) were evaluated as $4\pi \int_0^\infty \chi_j(r) dr$, *without* the factor of r^2 in the integrand. If we include the r^2 Jacobian, we obtain the expansion coefficients reported in Table I; for comparison we also give the coefficients originally published by SR.

The full SR pseudopotential combines V_R with a Coulomb potential from the classical point charges on each atom (tapered to zero with a cubic spline for the hydrogens) and an

TABLE I. Parameters that define the repulsive part of the SR pseudopotential, Eq. (3).

	j	n_j	ρ_j^a	B_j (SR)[a,b]	B_j (corr.)[a,c]
Oxygen	1	0	24.566	326 009.7	16 004.6
	2	0	14.078	2 768 832.	78 181.
	3	1	6.614	74 870.3	11 575.7
	4	1	4.101	−2 368.3	22 132.3
	5	2	2.835	1 735.8	−2 597.4
Hydrogen	1	0	1.890	−356.0	785.8
	2	0	2.835	1 171.9	436.8

[a]Energies in kcal mol^{-1}, lengths in Å.
[b]Published pseudopotential parameters (Ref. 1).
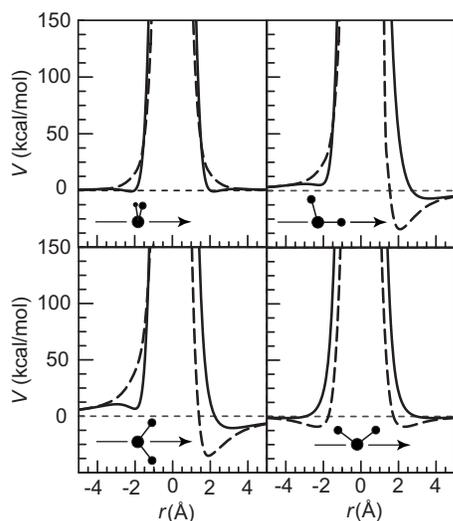[c]Corrected pseudopotential parameters.

FIG. 1. Representative cuts of the published (dashed curves) and corrected (solid curves) SR electron-water pseudopotentials along the directions indicated in each panel. As in Ref. 1, the potential includes a polarization term and point charges, with the Coulomb term on each hydrogen atom tapered to zero with a cubic spline.

oxygen-centered polarization term.[1] Figure 1 shows cuts of the full pseudopotential with the same Coulomb and polarization parameters used by SR for both the corrected (solid curves) and original (dashed curves) parameters B_j. The most significant changes in the pseudopotential from what was originally published are that the hydrogen atoms become much less attractive and that the oxygen-centered repulsion increases on the side of the molecule nearer the hydrogens.

To understand the importance of these changes, we have used mixed quantum/classical molecular dynamics simulation to study the ground-state hydrated electron with both the original and the corrected SR pseudopotentials. We placed the electron in a cubic box containing 200 water molecules in the NVE ensemble with a density of ~0.997 g/cc and an average T of 300 K. Equilibrium configurations for analysis were then taken every 100 fs from a 30 ps production run. We found the lowest four adiabatic eigenstates on a 16 $\times 16 \times 16$ grid that fills the box using techniques described in Ref. 5 and verified that the results do not change in a box with a 32^3 grid and 499 water molecules.

With the corrected pseudopotential, the hydrated electron occupies a nearly spherical cavity, but it has a radius of gyration of ~2.6 Å. Figure 2(a) shows that consistent with the larger radius, the calculated absorption spectrum with the corrected pseudopotential is redshifted, peaking at ~1.5 eV versus ~2.4 eV with the original SR pseudopotential,[1] placing the calculated spectrum in much better agreement with the ~1.7 eV peak seen experimentally.[3] In addition, Fig. 2(b) shows that the structure of the first solvation shell around the hydrated electron is quite different with the corrected pseudopotential: the O–H bonds of the first-shell water molecules no longer preferentially point directly toward the electron center of mass, and the first-shell structure is no longer quasioctahedral. Evidently, the greater repulsion of the oxygen center combined with the smaller attraction of the
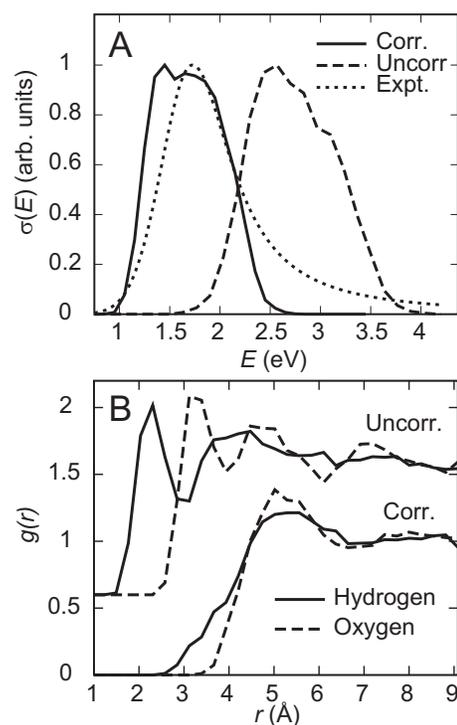

FIG. 2. Properties of the hydrated electron with both the published and corrected SR pseudopotentials. (a) Optical absorption spectra from the corrected (solid curve) and uncorrected (dashed curve) pseudopotentials. The dotted curve is the Gaussian–Lorenzian fit for the experimental hydrated electron absorption spectrum (Ref. 3). The simulated spectra do not show the blue tail seen in experiment because the calculations included only the lowest three excited states. (b) Electron center-of-mass radial distribution functions for water hydrogen (solid curves) and oxygen (dashed curves) sites. The results with the uncorrected SR pseudopotential have been shifted vertically for clarity.

hydrogen atoms does not favor the Kevan solvation motif.

Much of our molecular intuition about hydrated electrons has been based on simulations with the published SR pseudopotential. When this pseudopotential is corrected, however, the size, hydration structure, and spectroscopy of the hydrated electron change significantly. Given the approximations involved in deriving the SR pseudopotential, however, it is not clear how realistic one should expect the corrected SR pseudopotential to be. In view of the fact that the published SR potential can no longer be considered the result of a rigorous derivation, we agree with SR's Reply to this Comment[6] that in thinking about the properties of hydrated electrons, one should now view previously published SR-based simulations as arising from a well-tested, but *ad hoc*, model potential.

a)Electronic mail: schwartz@chem.ucla.edu.

[1] J. Schnitker and P. J. Rossky, J. Chem. Phys. **86**, 3462 (1987).
[2] L. Turi and D. Borgis, J. Chem. Phys. **117**, 6186 (2002).
[3] T. R. Tuttle, Jr. and S. Golden, J. Phys. Chem. **95**, 5725 (1991).
[4] L. Kevan, Acc. Chem. Res. **14**, 138 (1981).
[5] R. E. Larsen, M. J. Bedard-Hearn, and B. J. Schwartz, J. Phys. Chem. B **110**, 20055 (2006).
[6] J. Schnitker and P. J. Rossky, J. Chem. Phys. **131**, 037102 (2009).