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Technical Comment on “Does the Hydrated Electron Occupy a Cavity?” [Science 329, 65, (2010)]

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Abstract

Exact quantum mechanical calculations examining a recently implemented pseudopotential show that the results reported by Larsen et al. are based on a model that contains inaccuracies. We illustrate that, in contrast to the model used, the true electron-water interaction is repulsive in the region relevant to the reported extended electron distribution, consistent with the cavity model.

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The paper by Larsen, Glover and Schwartz (LGS) claims that an alternative physical picture of the hydrated electron model emerges from a series of mixed quantum-classical molecular dynamics simulations based on their new model (1). At the heart of the claim is the development of a new electron-water molecule pseudopotential by these authors that describes the interaction between the classically treated water molecules and the quantum mechanical excess electron. The authors correctly state that “A key element in any simulation of the hydrated electron is the electron-water interaction specified by the pseudopotential.”. In this comment we inspect the pseudopotential of LGS and show that inaccuracy in its description of the core region of the potential seriously undermines the credibility of the subsequent simulation results.

The following analysis applies protocols based on quantum mechanical model calculations similar in spirit to previous studies (2,3). We solve the Schroedinger equation for the excess electron in the field of the Hartree-Fock potential of a single water molecule (4) and a conveniently chosen repulsive potential (5). The repulsive potential confines the electron in the vicinity of the water molecule (here within an approximate sphere of $\sim 5 \text{ \AA}$ radius) and makes it possible to test the pseudopotential in the chemically most relevant region. The results of the exact calculations are compared to those using the reported pseudopotential (1,4), and also to a reference system of a free electron placed in the same repulsive potential. Since the energy and the electron density of the excess electron are sensitive to changes in the underlying potential, the comparison helps to pinpoint problems in the LGS pseudopotential.

The ground state energy for the reference system, a free electron confined by the repulsive potential is 4.6585×10^{-2} hartree (5,6). The exact solution of the excess electron Schroedinger equation, in the field of the water wave function *and* the confining potential, results in 5.0257×10^{-2} hartree. The more positive eigenenergy in the presence of the water

molecule immediately indicates that the average potential felt by the electron is repulsive in the vicinity of the water molecule. Although the difference in the energies is only ~ 0.1 eV, the impact of the underlying repulsion becomes significant in condensed phase simulations, as illustrated below. Replacing the exact electron-water potential by a rigorously derived pseudopotential in the Hamiltonian, one should obtain the same eigenenergy. The LGS potential, however, gives 4.5725×10^{-2} hartree (4). The lower energy relative to the reference system unequivocally confirms that instead of reproducing the average repulsion of the exact electron-water potential, the LGS potential is slightly attractive in the vicinity of the water molecule. The LGS model also badly fails to reproduce the electron density of the exact pseudo wave function (7) (Figure 1A). The significantly increased electron density on the oxygen side of the molecule by the LGS model relative to the exact density indicates that the LGS potential artificially introduces attraction here, while the depleted electron density on the hydrogen side suggests an opposite deviation, decreased attraction. The net result is the artificially attractive LGS potential. As directly related symptoms, suspicious regions appear in the reported pseudopotential that are not consistent with basic physical intuition. These include a relatively deep (~ 0.5 eV) attractive well in the molecular plane on the generally repulsive oxygen side of the molecule at ~ 3 Å from the oxygen and a repulsion in the generally attractive dipole direction on the hydrogen side at ~ 4 Å (see the inset of Figure 1B). At these distances one would expect simple electrostatics to dominate. These features are not shown in Figure 1 of Ref (1).

To demonstrate the serious consequences of an incorrect description of the core region in the LGS model, we performed quantum molecular dynamics simulations of a quantum mechanically treated electron in a classical water bath of 499 molecules, identical in setup to that described in Reference (1). In the simulation we employed a modified LGS parameter set, that is chosen by optimizing one parameter on the repulsive oxygen center in the original LGS

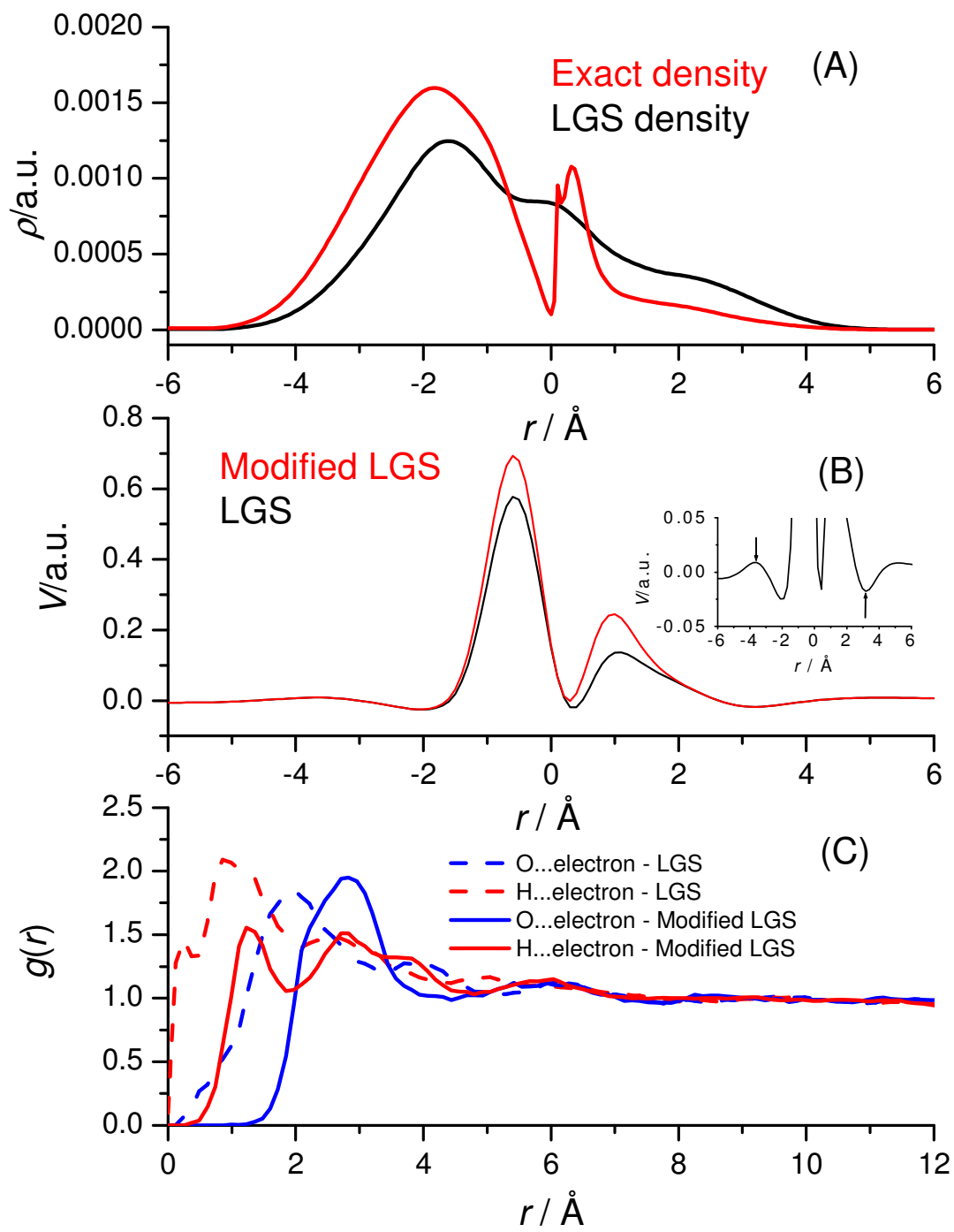
model to now reproduce the computed exact model eigenenergy (8). We note that this modification is minor (Figure 1B), similar in magnitude to the uncertainty of the numerical fitting of the LGS potential on the exact smoothed potential (1,9). The correction is nevertheless manifest in dramatically different properties of the hydrated electron compared to those of LGS (1). Most notably, the radial distribution functions testify the formation of a solvent cavity (Figure 1C) with a well-defined excluded volume around the electron (~ 0.5 Å radius for the hydrogen, ~ 1.5 Å radius for the oxygen), in sharp contrast to the LGS model. In parallel, the radius of the electron collapses to 2.3 Å from the LGS value of 2.6 Å indicating a more compact electron distribution. The vertical detachment energy (VDE) of the hydrated electron also undergoes a considerable change. The LGS potential predicts a VDE that is significantly higher (≥ 5 eV (1)) than experimental values of 3.3 eV (10a) and 3.6 eV (10b) or the ~ 4 eV simulation result using a pseudopotential consistent with a cavity based model (11). The simulation with the modified potential brings the VDE closer to the consensus range by 0.85 eV.

The present comment demonstrates that the electron-water pseudopotential of Larsen et al., although based on a rigorously derived potential surface, contains inaccuracies (12). The simulated properties of the hydrated electron are shown to be very sensitive to this problem. A simple introduction of a modified repulsion (by matching the exact energy of the quantum model) has been demonstrated to recover the traditional cavity picture, consistent with other pseudopotentials (3,13). The physical properties of the hydrated electron by Larsen et al., simulated on the incorrect potential, and the new structural characterization in particular, appear to be artifactual. Finally, we note that this cavity model of the hydrated electron is in accord with extensive, model free ab initio molecular dynamics simulations (14,15).

Figure Caption

Figure 1. (A) The electron density of the exact pseudo wave function (red) and the LGS electron density (black) along the dipole direction in the molecular plane through the oxygen atom. The center of mass of the water molecule is at the origin, the hydrogen atoms are at negative coordinates. (B) The repulsion modified pseudopotential (red) in the same molecular direction as above. For comparison the original LGS potential is also shown (black). The arrows in the inset show suspicious parts of the LGS potential. For clarity, the potentials do not contain the additive attractive polarization contributions. (C) Electron-hydrogen (red) and electron-oxygen (blue) radial distribution functions using the modified pseudopotential including polarization (solid curves). For comparison, the radial distribution functions obtained with the LGS potential (dashed) are also shown.

Figure 1. Turi and Madarász



References

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- (4) The model does not contain the polarization potential in the present approximation (2,3).
The same scheme was used at the development of the LGS potential (1). We note that the full potential including the *a posteriori* introduced polarization potential is used in the molecular dynamics simulations.
- (5) The repulsive potential, $V_{\text{conf}} = \frac{1}{2}k(x^8 + y^8 + z^8)$ where $k = 10^{-8}$ atomic unit, is centered on the water molecule center-of-mass (2,3). The repulsive potential hardly perturbs the potential energy surface at and around the water molecule, but erects a steep repulsive wall at $\sim 5 \text{ \AA}$ from the water molecule center-of-mass.
- (6) In the calculations, we use the same water geometry as Larsen et al. (1). The water wave function is evaluated at HF/6-31++G(d,p)+aug level (2,3). The basis set representing the excess electron consists of 86 Gaussian Lobe functions (transformed from the atom-centered 6-31++G(d,p)+aug basis set of the water molecule) and $7 \times 7 \times 7$ *s*-type functions (exponent 0.03) evenly distributed on a cubic grid of 20 bohr length centered on the water molecule (2,3). We verified that the calculations are converged with respect to the size of the distributed basis set.
- (7) The pseudo wave function was calculated as in References (1) and (2).
- (8) We changed the parameter B_2 from its original value of 0.209915 hartree to 0.34 hartree. The eigenenergy of the quantum model calculation changes from 4.5725×10^{-2} hartree to 5.0236×10^{-2} hartree. The exact value is 5.0257×10^{-2} hartree. The modified set keeps the qualitative shape of the LGS potential.

- (9) An example for an effect of similar magnitude is the increased repulsion between the hydrogen atoms penetrating in the attractive dipole direction in the fitted LGS potential relative to exact smoothed potential (see the top panel of Figure 1 of Ref. (1)).
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- (12) In addition, we also mention that the authors reported incorrect SPC charges in the LGS model ($-0.84 e$ for the oxygen atom instead of $-0.82 e$). We applied the correct charges. The choice does not influence the conclusions.
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