Supporting information for “A one-electron model for the aqueous electron that includes many-body electron–water polarization: Bulk equilibrium structure, vertical electron binding energy, and optical absorption spectrum”

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1 Fit parameters

The fit parameters that ultimately define the PEWP-2 model are given in Table 1. The nature of these parameters is described below.

- a_{ind}: Coulomb damping parameters for electrostatic interactions between the electron and the inducible dipoles, using the modified Coulomb operator defined in Eq. (7) of the paper. These parameters (one for the H-atom dipoles and one for the O-atom dipoles) are obtained by a fit to the MP2 polarization potential.

- a_{perm}: Coulomb damping parameters for electrostatic interactions between the electron and the permanent AMOEBA multipoles. These are fit, in conjunction with the repulsive potential, in order to reproduce the density maximum of the LRC-μBOP pseudo-wavefunction.

- B_i: These are parameters that define the repulsive potential, as defined in Eq. (10) of the paper. There is one set of parameters B_i (i = 1,2,3) for H and one set of O.

- c_i, z_i: These are parameters that are used to fit the exchange-correlation potential to a sum of atom-centered Gaussian functions, as in Eq. (9) of the paper. There is one set of each parameter for the O sites and one set for the H sites.

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Parameter	Atomic site	Value (atomic units)
a_{ind}	oxygen	1.47027
a_{perm}	oxygen	1.077362
a_{ind}	hydrogen	0.514081
a_{perm}	hydrogen	0.840234
B_1	oxygen	1.035565
B_2	oxygen	0.999428
B_3	oxygen	0.40954
B_1	hydrogen	0.4
B_2	hydrogen	1.010174
B_3	hydrogen	0.463554
c_1	oxygen	−0.226083
c_1	hydrogen	−0.7930992
c_2	hydrogen	−0.03180506
c_3	hydrogen	0.892828395
z_1	oxygen	0.18013656
z_1	hydrogen	2.19453033
z_2	hydrogen	0.12620980
z_3	hydrogen	2.76886142

Table 1: Parameters that define the PEWP-2 model.

2 Additional cluster benchmarks

2.1 Relative isomer energies

While the MP2/6-31(1+,3+)G* method affords accurate VEBEs, due to a lack of strong correlation effects and absence of significant orbital relaxation upon electron detachment,[1] accurate benchmarks for relative conformational energies demand a higher level of theory. To assess how well the model predicts the relative energies of $(H_2O)_n^-$ cluster isomers, we use MP2/CBS benchmarks, where "CBS" indicates extrapolation to the complete-basis limit, as described in our previous work.[2] Geometries for the benchmark clusters ($n = 4, 5, 6$) were optimized on the anion surface at the B3LYP/6-31(1+,3+)G* level, and were then re-optimized using the model potentials, in order to compare the relative energetics. We compare both the relative energies of the anion isomers, and also the relative energies of the neutral clusters at the same geometries, as the latter provides a sense of how well the neutral potential surface is described at typical anion geometries. The full set of isomer geometries is depicted in Ref. 2.

Figures 1, 2, and 3 show the relative energy comparisons for n = 4, 5, and 6, respectively. For the tetramers, all of the model potentials reproduce the *ab initio* data surprisingly well, for both the neutral and anionic clusters. For the pentamers, however, only the polarizable models (PEWP-1 and PEWP-2) track the *ab initio* data well. In particular, the TB models gives a relatively poor

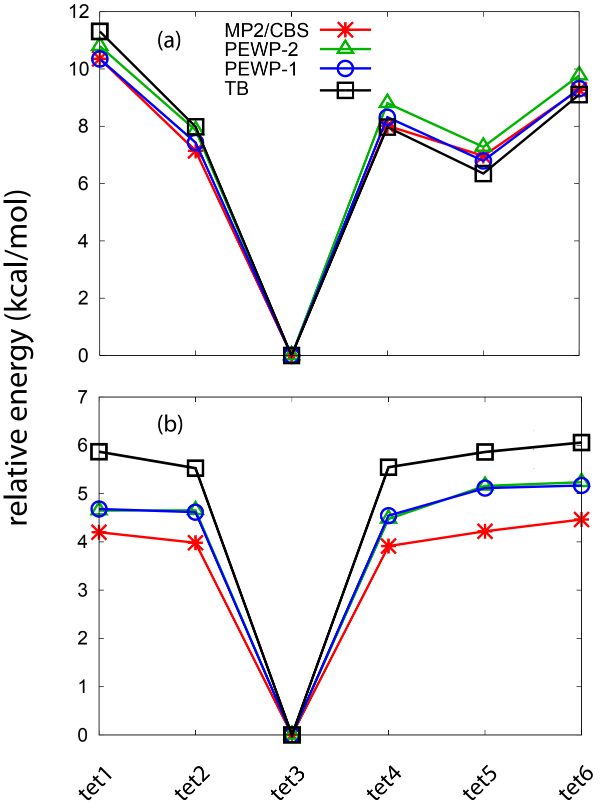

Figure 1: Relative energies of (a) $(H_2O)_4$ cluster isomers and (b) $(H_2O)_4^-$ isomers at the same geometries, which represent stationary points on the anion potential energy surface. *Ab initio* geometries are from B3LYP/6-31(1+,3+)G*.

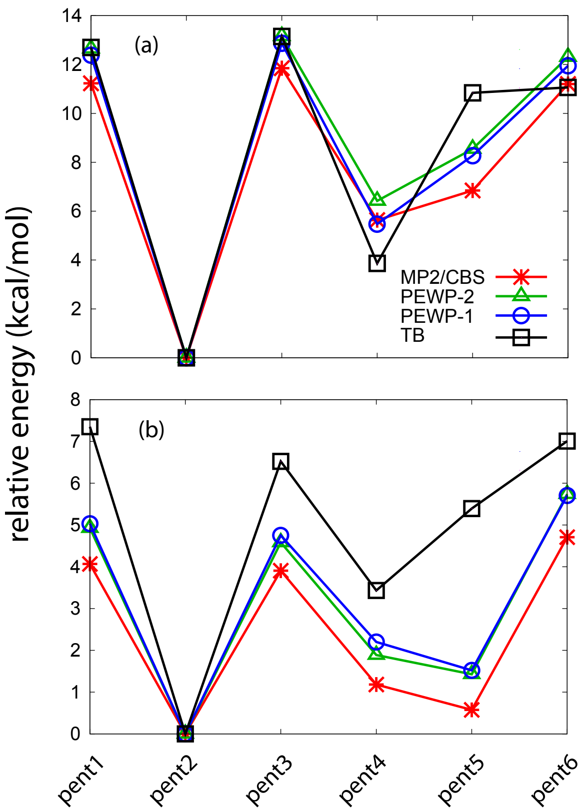

Figure 2: Relative energies of (a) $(H_2O)_5$ cluster isomers and (b) $(H_2O)_5^-$ isomers at the same geometries, which represent stationary points on the anion potential energy surface. *Ab initio* geometries are from B3LYP/6-31(1+,3+)G*.

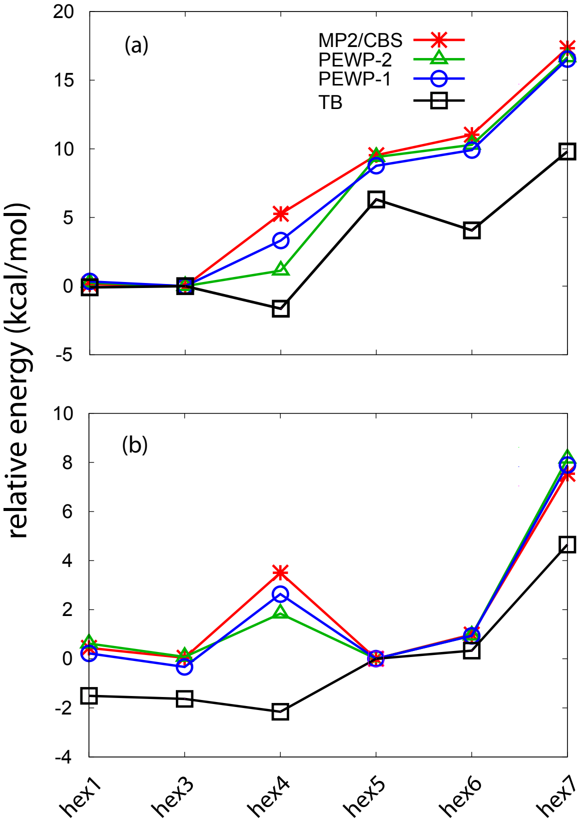

Figure 3: Relative energies of (a) $(H_2O)_6$ cluster isomers and (b) $(H_2O)_6^-$ isomers at the same geometries, which represent stationary points on the anion potential energy surface. *Ab initio* geometries are from B3LYP/6-31(1+,3+)G*.

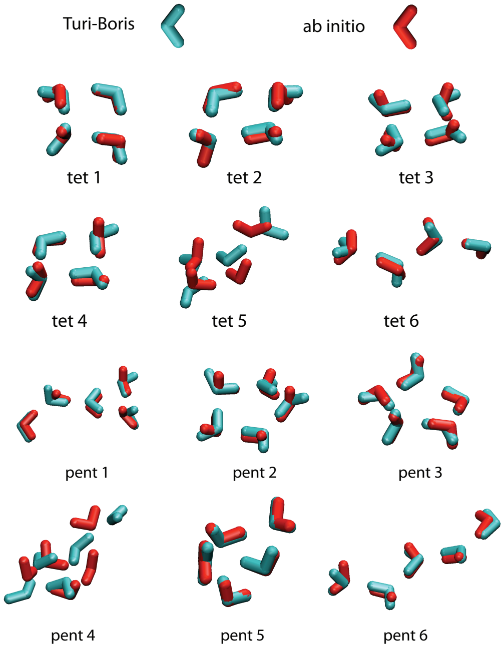

Figure 4: Comparison of *ab initio* and TB geometries for the tetramer structures studied in this work. Geometries were optimized on the anion potential energy surface, and *ab initio* geometries are from B3LYP/6-31(1+,3+)G*.

description of the isomer "pent-5", placing it too high in energy by ∼5 kcal/mol in both the anion and neutral case. This poor description does not arise from any deficiency in the electron-water interactions, but is due to the underlying water model, SPC, as discussed below.

A comparison is made in Fig. 4 between the *ab initio* optimized geometries and those obtained using the TB model. Geometries from the PEWP-1 and PEWP-2 models are not shown, as they are nearly identical to the *ab initio* geometries. Optimization on the TB surface tends to rotate non-hydrogen-bonded (dangling) hydrogen atoms such that the water molecules lie in planes. Good examples of this are the isomers "tet-3" where all waters have been rotated into a plane, and "tet-5" where the three-dimensional cage-type structure collapses onto a plane. This rotation into planes seems not to affect the relative energies of the tetramers, although it does effect the pentamer and hexamer energies. In particular, the only geometry in which this rotation does not occur is pent-5. The waters in this geometry are not able to rotate because all of the hydrogen atoms, save for those associated with the "double acceptor" ("AA")

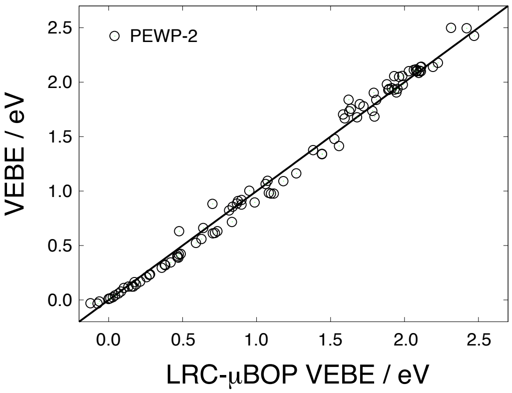

Figure 5: Correlation of VEBEs computed using PEWP-2 with LRC-μBOP.

water molecule, are involved in hydrogen bonds, and the aforementioned rotation would break these bonds. This apparently leaves this geometry quite high in energy.

As discussed previously,[2] we believe the source of this planarity problem is the lack of out-of-plane electrostatics. Effectively, the point charge water molecules are rotating into planes because they are aligning dipoles which must only have components in the plane of the molecule. This rotation does not occur with the AMOEBA model because it contains quadrupole (and induced dipole) components that do not lie in the plane of the water molecule. The SPC model is missing weaker electrostatic forces that stabilize non-planar configurations in the *ab initio* and PEWP-2 geometries.

2.2 VEBE of PEWP-2 compared to LRC-μBOP

Finally, we compare VEBEs computed with PEWP-2 to those obtained using LRC-μBOP. This comparison (see Fig. 5) is made over our full database of 95 cluster geometries. The average absolute error for PEWP-2 compared to LRC-μBOP is 0.059 eV, however the average signed error is only -0.003 eV instead of -0.020 eV when compared to MP2. This indicates that, on average, the binding energies of PEWP-2 are in very good agreement with this density functional. This agreement is ultimately a sort of self-consistency check, since the exchange-correlation potential used to parameterize PEWP-2 was obtained from the LRC-μBOP functional.

References

[1] J. M. Herbert and M. Head-Gordon, Phys. Chem. Chem. Phys. **8**, 68 (2005).

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