Molecular Potential Energy Surfaces in Many Dimensions

Edited by

Mark M. Law
Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, United Kingdom

Andreas Ernesti
Auf Debert 12, 54595 Schlossheck, Germany

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Molecular Potential Energy Surfaces in Many Dimensions

The role of the *neutral* water potential in determining the properties of *anionic* water clusters

John M. Herbert, Leif D. Jacobson, and Christopher F. Williams
Department of Chemistry, The Ohio State University, Columbus, OH 43210

Introduction

The hydrated electron, e^-_{aq}, has been a subject of interest in the chemical physics community ever since its absorption spectrum was first measured in 1962 [1]. Models of this species based on one-electron pseudopotentials appeared not long after that [2], and by the mid-1980s, computer power and computational quantum mechanics algorithms had advanced to such a point that atomistic simulations could be performed on e^-_{aq} and also finite water cluster anions, $(H_2O)^-_n$, by treating just the unpaired electron quantum-mechanically. Hydrated-electron clusters are perhaps *the* prototypical system for studying the interplay between quantum mechanics (essential for the treatment of the delocalized excess electron, and computationally tractable using one-electron model Hamiltonians or one-electron path integral simulations) and statistical mechanics (also mandatory, due to the large number of near-degenerate local minima in water clusters). As such, many different groups have taken a stab (or multiple stabs) at designing an electron–water pseudopotential for use in such simulations[3–15].

Although anionic water clusters may serve as useful, finite models of e^-_{aq}, the clusters are in some ways more interesting than the bulk, especially from the standpoint of potential energy surfaces. Small clusters are amenable to *ab initio* electronic structure calculations that can be used to assess various analytic potentials, and we have reported such *ab initio* benchmarks up to $n = 33$ [16–18]. Moreover, clusters offer a wider range of morphologies and electron-binding motifs, and thus pose stringent tests of our ability to model the fundamental electron–molecule and molecule–molecule interactions. In short, we study clusters because

they are *not* like the bulk. [One of us (J.M.H.) first heard this sentiment expressed by Carl Lineberger, whom the authors warmly acknowledge.]

Any sufficiently large $(H_2O)_n^-$ cluster ($n = 24$ is large enough [18]) will exhibit certain local potential energy minima that correspond to an internally-bound (cavity-bound) electron, and also local minima in which the unpaired electron is bound at the surface of the cluster. In addition, sub-motifs such as binding to a double acceptor ("AA") water molecule can be identified in both surface and cavity isomers. Which of these binding motifs is observed experimentally has been a subject of debate for two decades [19–25] with experimentalists usually arguing for evidence of cavity-like solvation as early as $n = 11$ [20, 21], but with pseudopotential simulations repeatedly finding that cavity-bound isomers are only dynamically stable in much large clusters ($n \gtrsim 60$ at least [19], and perhaps $n \gtrsim 200$ at $T = 300$ K [23]). Which isomers will be observed depends upon a subtle balance between water–water hydrogen-bond interactions and the electron–water interaction, since the latter provides a strong driving force for creation of "dangling" hydrogen atoms that disrupt the hydrogen-bond network. (The significance of this driving force may be inferred from the observation that, of all known ions, only e^- has a positive entropy of hydration; it is the "champion structure breaker" [26]). In addition, we have shown that dynamical electron correlation is much more significant in cavity isomers than in surface isomers [18]. A balanced description of these various effects using a one-electron pseudopotential may prove challenging.

Electron–water interaction potentials

Early (and some later) attempts to model the electron–water interaction proceeded somewhat haphazardly. Frequently, this interaction was taken to consist of truncated or damped charge–charge interactions between e^- and the H_2O partial atomic charges, plus a short-range repulsive potential and a polarization potential of the form $V_{\mathrm{pol}} \propto -r^{-4}$, where r is the electron–water distance. Although such models may afford sensible results for some properties of $(H_2O)_n^-$, the addition of a large, stabilizing electron–hydrogen Coulomb interaction is often more than simple water models can bear, and a close inspection reveals catastrophic flaws in the resulting potential energy surfaces, which to our knowledge have not previously been reported.

One example may be found in the recently-developed electron–water interaction potential developed by Joannopoulos and co-workers [9, 27], which consists of precisely the terms indicated above, and is parameterized for use with the Lie–Clementi water potential [28]. A serious flaw in this potential – unmentioned by Joannopoulos and co-workers – is illustrated in Fig. 1, which depicts the H–O–H bending potential for neutral H_2O (that is, the Lie–Clementi water bend potential) alongside the bending potential for H_2O^- when the electron sits a fixed distance of 0.23 Å away from one hydrogen atom, along the O–H bond vector. (This distance represents the potential minimum for the e^- along the O–H bond vector, with H_2O fixed to its minimum-energy geometry.) Although the Lie–Clementi H_2O potential has a large (~ 2 eV) barrier to linearity, in H_2O^- the electron–hydrogen interaction is sufficiently attractive so that the minimum-energy bond angle is $\approx 0°$!

Another lurking catastrophe can be identified in the pseudopotential developed by Turi and Borgis [10], which has been used in several recent (and controversial [25]) simulations of $(H_2O)_n^-$ [23, 29–32]. Although this potential is based upon a careful analysis of the electron–water interaction [33], in the studies cited above it is used in conjunction with the simple point charge (SPC) water potential [34]. The flexible version of the SPC potential includes parameters for both harmonic and Morse O–H stretch potentials, and (with an eye toward vibrational spectroscopy) we originally implemented the Turi–Borgis/SPC model using the latter.

The O–H stretch potential for SPC water is depicted in Fig. 2 (solid curve). Although this potential does erroneously turn over at very large O–H distances, as a result of a stretch–bend coupling term with a negative coefficient, in neutral water this turnover is far too high in energy to cause problems. Addition of an extra electron, however, significantly reduces the O–H stretching barrier, as shown in the dashed curve in Fig. 2. (To generate this potential energy curve, we fixed the electron at a distance of 0.35 Å from one hydrogen atom, along the O–H bond vector. This distance represents the minimum in the electron–water interaction potential along the O–H bond vector, when H_2O is fixed at its minimum-energy geometry.) Although the dissociation barrier is still large (0.3 eV, or about 10 k_BT at $T = 300$ K), we were nevertheless unable to perform Monte Carlo or path integral calculations on this potential, due to problems with H_2O dissociation.

Obviously, we could give up on using flexible monomers, and thus

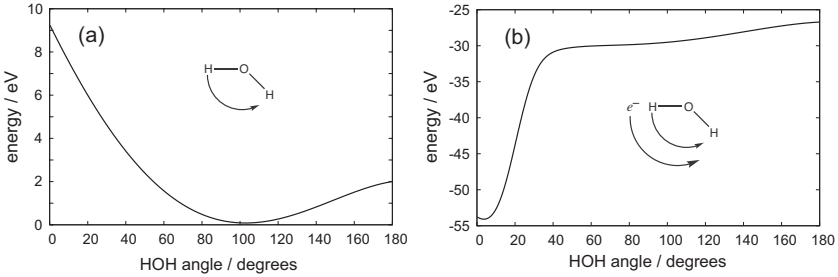

FIG. 1: Bending potentials for (a) H_2O and (b) H_2O^-, according to the model potential of Park *et al* [9]. In (b), the e^- sits a fixed distance of 0.23 Å from one H atom along the corresponding O–H bond vector.

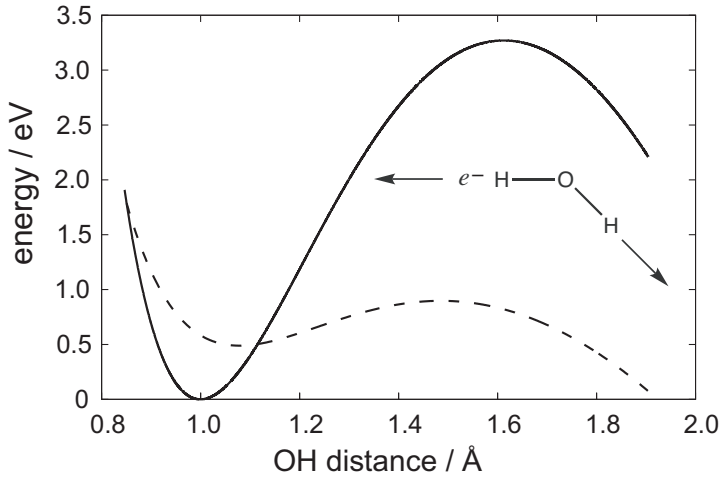

FIG. 2: Stretching potentials for H_2O (solid line) and H_2O^- (dashed line), according to the Turi–Borgis electron–water potential [10], used in conjunction with Morse version of the flexible SPC water model [34]. In H_2O^-, the e^- sits a fixed distance of 0.35 Å from one H atom, along one O–H bond vector.

perform simulations that are sensible (at least ostensibly), but the fact that these intramolecular water potentials are unable to cope with the strong electrostatic interactions engendered by the electron–water potential gives us pause.

Problems with oversimplified analytic potentials aside, there is good reason to suspect that a high-quality water model is a minimum requirement for a realistic $(H_2O)_n^-$ model. Our own *ab initio* calculations in small clusters reveal that, very often, the neutral $(H_2O)_n$ potential energy surface plays a larger role in determining the vertical electron binding energy (VEBE) than does the anionic $(H_2O)_n^-$ potential surface [35]. As an example, relative energies of several $(H_2O)_4^-$ isomers are depicted in Fig. 3. Isomers A, B/D, and C are identifiable as distinct features in the experimental photoelectron spectrum of this cluster [36], which we have simulated using *ab initio* molecular dynamics [35]. (Isomer D is not resolvable from B.)

Note that isomers A, B, and D of $(H_2O)_4^-$ (each of which exhibits the AA binding motif) are essentially iso-energetic, yet have fairly different VEBEs owing to sizable energy differences among the underlying neutral water tetramers. *Ab initio* molecular dynamics simulations [35] reveal that, although these anionic clusters are stable at $T = 300$ K, they rapidly ($\tau \sim$ 100–200 fs) isomerize upon electron detachment to form the (non-AA) neutral analogue of isomer C, which closely resembles the global minimum on the $(H_2O)_4$ potential surface. These observations indicate that the points A, B, and D are quite removed from any stationary point on the *neutral* $(H_2O)_4$ potential energy surface.

Given the role of e^- as the "champion structure-breaker" [26], it should come as no surprise that the electron–water interaction stabilizes water networks that would be extremely unstable (and very high in energy) as neutral water clusters. AA-type isomers of $(H_2O)_n^-$ are just one example. Such structures are not accessible in neutral liquid water under ordinary thermodynamic conditions, and thus the performance of simple water potentials for such geometries is highly suspect. Indeed, simple water potentials such as SPC are sometimes unreliable even for neutral $(H_2O)_n$ clusters [37], even while they are reasonably accurate for bulk liquid water. This is just one example of how cluster data place stringent demands on analytic potential models.

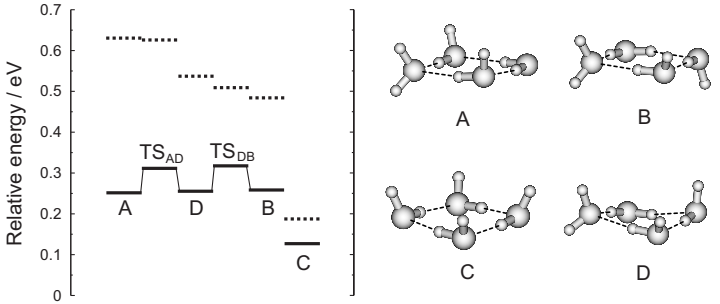

FIG. 3: Minima (A, B, C, and D) and transition states (TS_{AD} and TS_{DB}) on the potential energy surface of $(H_2O)_4^-$ (solid horizontal lines). All four local minima are identifiable in the experimental photoelectron spectrum [35, 36]. [The level of theory is MP2/6-31(1+,3+)G*//B3LYP/6-31(1+,3+)G* [16].] The corresponding points on the $(H_2O)_4$ potential surface (broken lines) are not stationary points, but they are mainly responsible for the vertical electron binding energy. Zero energy corresponds to the global minimum of $(H_2O)_4$, which is not shown.

A new hydrated-electron model

The results above argue strongly in favour of using a polarizable water potential, as only polarizable models give accurate results for $(H_2O)_n$ clusters [37]. There have been several recent efforts to parameterize hydrated-electron potentials using polarizable water models [12–15], but so far there has been little in the way of systematic analysis of how the choice of water model manifests in the predicted structure and spectroscopy of $(H_2O)_n^-$ clusters. (One exception is a finite-temperature Monte Carlo study of $(H_2O)_6^-$, in which a change in water models is shown to shift the distribution away from AA-type isomers [13]).

As a first step toward such a systematic analysis, we have reparameterized the electron–water interaction potential of Turi and Borgis [10] substituting the AMOEBA water potential [38] in place of SPC. Electrostatic interactions in the AMOEBA potential are handled

by means of atom-centered charges, dipoles, and quadrupoles, with the dipoles having both permanent and flexible components. The flexible (induced) parts of the atom-centered dipoles are determined self-consistently. Details of the fitting procedure and our implementation will be discussed in a future publication.

The essential feature of this approach is that we have combined a careful treatment of the electron–water interaction (*a la* Turi and Borgis [10]) with a careful treatment of the water–water interactions (*a la* Ren and Ponder [38]). Figure 4 compares VEBEs predicted by the new model, and also the Turi–Borgis model, to *ab initio* benchmarks, for two databases of $(H_2O)_n^-$ isomers [17, 18] that consist of a total of 74 geometries ranging from $n = 2$ to $n = 33$. The root-mean-square difference in VEBEs between the new model and the benchmark values is only 0.083 eV, as compared to 0.193 eV for the Turi–Borgis model. We emphasize that the parameters in the new model were fit to reproduce the electron–water interaction, not the VEBEs directly, whereas the parameters in the AMOEBA water model were fit (by Ren and Ponder [38]) to reproduce the water–water interactions.

It remains to explore how the new hydrated-electron model performs for other properties, such as the e_{aq}^- absorption spectrum, and such tests are underway in our group. More importantly, because the new pseudopotential model has a form that parallels that of the Turi–Borgis model, we can make direct and meaningful comparisons between the two, and we are currently performing parallel, systematic studies of these two pseudopotential models, in an effort to gain a detailed understanding of how the neutral water potential energy surface manifests structurally and spectroscopically in $(H_2O)_n^-$ clusters and in bulk e_{aq}^-.

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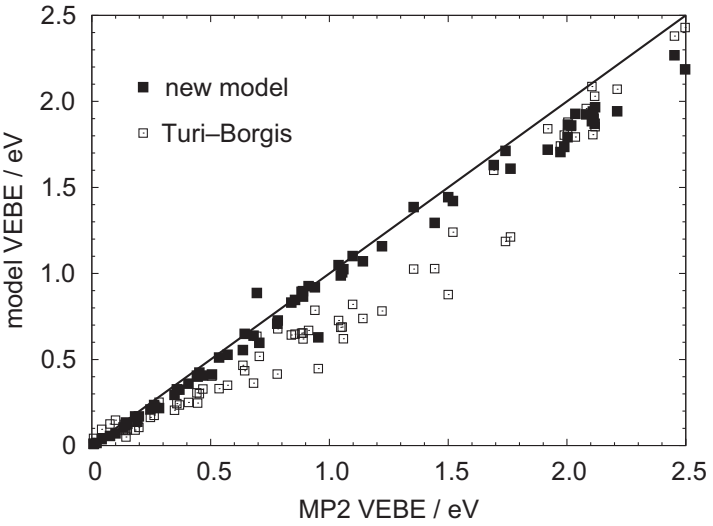

FIG. 4: VEBEs predicted by the Turi–Borgis model [10] and the new model (this work), for two databases [17, 18] of $(H_2O)_n^-$ cluster isomers that include both surface and cavity isomers, ranging from $n = 2$ to $n = 33$. The solid line depicts the diagonal along which the MP2/6-31(1+,3+)G* VEBE equals the model Hamiltonian VEBE.

REFERENCES

[1] E. J. Hart and J. W. Boag, "Absorption spectrum of the hydrated electron in water and in aqueous solutions", J. Am. Chem. Soc. **84**, 4090 (1962).

[2] J. Jortner and S. A. Rice, "Theoretical studies of solvated electrons," in *Solvated Electron*, edited by R. F. Gould, volume 50 of *Advances in Chemistry*, chapter 2, pages 7–26, American Chemical Society Publications, Washington, D.C., 1965.

[3] C. D. Jonah, C. Romero, and A. Rahman, "Hydrated electron revisited via the Feynman path integral route", Chem. Phys. Lett. **123**, 209 (1986).

[4] A. Wallqvist, D. Thirumalai, and B. J. Berne, "Localization of an excess electron in water clusters", J. Chem. Phys. **85**, 1583 (1986).

[5] A. Wallqvist, D. Thirumalai, and B. J. Berne, "Path integral Monte Carlo study of the hydrated electron", J. Chem. Phys. **88**, 6404 (1987).

[6] J. Schnitker and P. J. Rossky, "An electron-water pseudopotential for condensed phase simulation", J. Chem. Phys. **86**, 3462 (1987).

[7] R. N. Barnett, U. Landman, and C. L. Cleveland, J. Jortner "Surface States of Excess Electrons on Water Clusters", Phys. Rev. Lett. **59**, 811 (1987).

[8] R. N. Barnett, U. Landman, C. L. Cleveland, and J. Jortner, "Electron localization in water clusters. I. electron water pseudopotential", J. Chem. Phys. **88**, 4421 (1988).

[9] I. Park, K. Cho, S. Lee, K. S. Kim, and J. D. Joannopoulos, "Ab initio atomistic dynamical study of an excess electron in water", Comp. Mat. Sci. **21**, 291 (2001).

[10] L. Turi and D. Borgis, "Analytical investigations of an electronwater molecule pseudopotential. II. Development of a new pair potential and molecular dynamics simulations", J. Chem. Phys. **117**, 6186 (2002).

[11] F. Wang and K. D. Jordan, "Application of a Drude model to the binding of excess electrons to water clusters", J. Chem. Phys. **116**, 6973 (2002).

[12] T. Sommerfeld and K. D. Jordan, "Quantum Drude oscillator model for describing the interaction of excess electrons with water clusters: an application to $(H_2O)_{13}^-$", J. Phys. Chem. A **109**, 11531 (2005).

[13] T. Sommerfeld, S. D. Gardner, A. DeFusco, and K. D. Jordan, "Low-lying isomers and finite temperature behaviour of $(H_2O)_6^-$," J. Chem. Phys. **125**, 174301 (2006).

[14] A. DeFusco, T. Sommerfeld, and K. D. Jordan, "Parallel tempering Monte Carlo simulations of the water heptamer anion," Chem. Phys. Lett. **455**, 135 (2008).

[15] J. E. Aremu-Cole, *Mixed quantum-classical study of a hydrated electron and investigation of temperature-control algorithms*, PhD thesis, Clemson University, 2007.

[16] J. M. Herbert and M. Head-Gordon, "Calculation of electron detachment energies for water cluster anions: An appraisal of electronic structure methods, with application to $(H_2O)_{20}^-$ and $(H_2O)_{24}^-$", J. Phys. Chem. A **109**, 5217 (2005).

[17] J. M. Herbert and M. Head-Gordon, "Accuracy and limitations of

second-order many-body perturbation theory for predicting vertical detachment energies of solvated-electron clusters", Phys. Chem. Chem. Phys. **8**, 68 (2006).

[18] C. F. Williams and J. M. Herbert, "Influence of structure on electron correlation effects and electron-water dispersion interactions in anionic water clusters," J. Phys. Chem. A **112**, 6171 (2008).

[19] R. N. Barnett, U. Landman, C. L. Cleveland, and J. Jortner, "Electron Localization in Water Clusters. II. Surface and Internal States," J. Chem. Phys. **88**, 4429 (1988).

[20] J. V. Coe, G. H. Lee, J. G. Eaton, S. T. Arnold, H. W. Sarkas, K. H. Bowen, C. Ludewigt, H. Haberland, and D. R. Worsnop, "Photoelectron spectroscopy of hydrated electron cluster anions, $(H_2O)^-_{n=2-69}$", J. Chem. Phys. **92**, 3960 (1990).

[21] J. V. Coe, S. T. Arnold, J. G. Eaton, G. H. Lee, and K. H. Bowen, "Photoelectron spectra of hydrated electron clusters: Fitting line shapes and grouping isomers", J. Chem. Phys. **125**, 014315 (2006).

[22] D. M. Bartels, "Moment analysis of hydrated electron cluster spectra: Surface or internal states?", J. Chem. Phys. **115**, 4404 (2001).

[23] L. Turi, W.-S. Sheu, and P. J. Rossky, "Characterization of excess electrons in water-cluster anions by quantum simulations", Science, **309**, 914 (2005).

[24] J. R. R. Verlet, A. E. Bragg, A. Kammrath, O. Cheshnovsky, and D. M. Neumark, "Observation of Large Water-Cluster Anions with Surface-Bound Excess Electrons", Science **307**, 93 (2005).

[25] J. R. R. Verlet, A. E. Bragg, A. Kammrath, O. Cheshnovsky, and D. M. Neumark, "Comment on 'Characterization of excess electrons in water-cluster anions by quantum simulations" Science **310**, 1769 (2005).

[26] P. Han and D. M. Bartels, "Reevaluation of Arrhenius parameters for H+ OH^- $\rightarrow (e^-)_{aq}$+ H_2O and the enthalpy and entropy of hydrated electrons", J. Phys. Chem. **94**, 7294 (1990).

[27] M. Skorobogatiy, I. J. Park, and J. D. Joannopoulos, "The nature of a floating electron", Comp. Mat. Sci. **32**, 96 (2005).

[28] G. C. Lie and E. Clementi, "Molecular-dynamics simulation of liquid water with an *ab initio* flexible water-water interaction potential", Phys. Rev. A **33**, 2679 (1986).

[29] L. Turi, Á. Madarász, and P. J. Rossky, "Excess electron localization

sites in neutral water clusters", J. Chem. Phys. **125**, 014308 (2006).
[30] D. Borgis, P. J. Rossky, and L. Turi, "Quantized time correlation function approach to nonadiabatic decay rates in condensed phase: Application to solvated electrons in water and methanol", J. Chem. Phys. **125**, 064501 (2006).
[31] D. Borgis, P. J. Rossky, and L. Turi, "Nuclear quantum effects on the nonadiabatic decay mechanism of an excited hydrated electron", J. Chem. Phys. **127**, 174508 (2007).
[32] Á. Madarász, P. J. Rossky, and L. Turi, "Excess electron relaxation dynamics at water/air interfaces", J. Chem. Phys. **126**, 234707 (2007).
[33] L. Turi, M.-P. Gaigeot, N. Levy, and D. Borgis, "Analytical investigations of an electronwater molecule pseudopotential", I. Exact calculations on a model system J. Chem. Phys. **114**, 7805 (2001).
[34] K. Toukan and A. Rahman, "Molecular-dynamics study of atomic motions in water", Phys. Rev. B **31**, 2648 (1985).
[35] J. M. Herbert and M. Head-Gordon, "First-principles, quantum-mechanical simulations of electron solvation by a water cluster", Proc. Natl. Acad. Sci. USA **103**, 14282 (2006).
[36] J.-W. Shin, N. I. Hammer, J. M. Headrick, and M. A. Johnson, "Preparation and photoelectron spectrum of the 'missing' $(H_2O)_4$ cluster", Chem. Phys. Lett. **399**, 349 (2004).
[37] G. S. Fanourgakis, E. Aprá, and S. S. Xantheas, "High-level *ab initio* calculations for the four low-lying families of minima of $(H_2O)_{20}$. I. Estimates of MP2/CBS binding energies and comparison with empirical potentials", J. Chem. Phys. **121**, 2655 (2004).
[38] P. Ren and J. W. Ponder, "Polarized atomic multipole water model for molecular mechanics simulation", J. Phys. Chem. B **107**, 5933 (2003).