## Supporting Information for

# Specific Reaction Path Hamiltonian for Proton <br> Transfer in Water: Re-parameterized Semi- <br> Empirical Models 

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Table S1. Description of the optimized parameters for the semi-empirical methods.

| Parameters $^{a}$ | MNDO-based | OM $x$ |
| :--- | :---: | :---: |
| (AM1 and | $(x=1,2$ |  |
| Slate-type orbital exponents $\zeta_{\mathrm{s}}, \zeta_{\mathrm{p}}$ | $\mathrm{PM} 3)$ | and 3) |
| Scale factor for the Gaussian-type orbitals $\zeta$ | Y | N |
| One-electron one-center integrals $U_{\mathrm{ss}}, U_{\mathrm{pp}}$ | N | Y |
| One-electron two-center integral parameters $\beta_{\mathrm{s}}, \beta_{\mathrm{p}}$ | Y | Y |
| One-electron two-center integral parameters $\beta_{\mathrm{s}}, \beta_{\mathrm{p}}, \beta_{\pi}, \alpha_{\mathrm{s}}, \alpha_{\mathrm{p}}, \alpha_{\pi}$ | N | Y |
| Two-electron one-center integrals $G_{\mathrm{ss}}, G_{\mathrm{pp}}, G_{\mathrm{sp}}, G_{\mathrm{p} 2}, H_{\mathrm{sp}}$ | Y | Y |
| Atomic core-core repulsion term parameters $\alpha$ | Y | Y |
| Gaussian core repulsion function parameters $K, L, M$ | Y |  |
| Pre-factors for orthogonalization corrections $F, G$ | N | N |

${ }^{a}$ Parameters are optimized for oxygen and hydrogen, for which the total number of parameters is 32 for AM1, 29 for PM3, 27 for OM1, 31 for OM2, and 27 for OM3, respectively. Note that the parameters $\beta_{\mathrm{s}}$ and $\beta_{\mathrm{p}}$ are defined differently in the MNDO-based and orthogonalization-corrected methods.

Table S2. Location of minima and maxima in the radial distribution functions for bulk water.

|  | $g_{\mathrm{OO}}(r)^{a}$ |  |  | $g_{\mathrm{OH}}(r)^{a}$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $1{ }^{\text {st }}$ Max. | $1^{\text {st }}$ Min. | $2^{\text {nd }}$ Max. | $1{ }^{\text {st }}$ Max. | $1^{\text {st }}$ Min. | $2^{\text {nd }}$ Max. |
| Exp. ${ }^{\text {b }}$ | 2.76 | 3.42 | 4.47 | 1.71 | 2.43 | 3.33 |
| AM1 | 2.75 | 3.85 | n/a | 2.25 | 2.85 | 3.45 |
| AM1n | 2.75 | 3.90 | n/a | 2.25 | 2.75 | 3.45 |
| PM3 | 2.75 | 4.05 | $\mathrm{n} / \mathrm{a}$ | 1.85 | 2.25 | 3.25 |
| PM3n | 2.75 | 4.15 | $\mathrm{n} / \mathrm{a}$ | 1.75 | 2.25 | 3.25 |
| OM1 | 2.85 | 3.85 | $\mathrm{n} / \mathrm{a}$ | 2.25 | 2.60 | 3.45 |
| OM1n | 2.85 | 3.85 | n/a | 2.25 | 2.55 | 3.35 |
| OM3 | 2.35 | 3.15 | 3.95 | n/a | 2.30 | 2.95 |
| OM3n | 2.75 | 3.45 | 4.75 | 1.85 | 2.45 | 3.35 |

${ }^{a}$ In $\AA$. The maximum corresponding to the covalently bound hydrogen is excluded from $g_{\mathrm{OH}}(r)$. See Fig. 7 and Fig. 8 in the text for the RDF curves.
${ }^{b}$ Soper, A. K. Chem. Phys. 2000, 258, 121-137; Soper, A. K.; Benmore, C. J. Phys. Rev. Lett. 2008, 101, 065502/1-4.

## Figure S1: Radial distribution functions $g_{\circ \circ}(r)$ for water at the MM level

Radial distribution functions $g_{\mathrm{OO}}(r)$ for water computed for the (A) SPC and (B) TIP3P water models. PBC indicates simulations employing periodic boundary conditions. The experimental data (Exp) is plotted in both panels for comparison. Note that all curves have been scaled such that the height of the first peak is 1.00 .


Figure S2: Radial distribution functions $g_{\text {он }}(r)$ for water at the MM level

Radial distribution functions $g_{\mathrm{OH}}(r)$ for water computed for the (A) SPC and (B) TIP3P water models. PBC indicates simulations employing periodic boundary conditions. The experimental data (Exp) is plotted in both panels for comparisons. Note that all curves have been scaled such that the height of the second peak in the graph (near $3.3 \AA$ ) is 1.00 .


## Figure S3: Optimized Eigen cation

Superimposition of the optimized geometries of the Eigen cation (Entry (g) in Fig. 1). The alignment is based on the hydronium ion coordinates. Color code for the geometries: MP2 in red, authentic semi-empirical methods in green, and re-parameterized semi-empirical models in blue. Distances in $\AA$ and angles in degree.
(A) PM6

(B) AM1

(C) PM3
(D) OM1

(E) OM2
(F) OM3


## Figure S4: Optimized water tetramer

Superimposition of the optimized geometries of the water tetramer (Entry (h) in Fig. 1). The alignment is based on all atomic coordinates. See caption of Fig. S3 for conventions.
(A) MP2

(C) PM3n

(E) OM2n

(B) AM1n

(D) OM1n

(F) OM3n


## Figure S5: Optimized Zundel ion in complex with two water molecules

Superimposition of the optimized Zundel ion in complex with two water molecules (Entry (i) in Fig. 1). The alignment is based on the Zundel ion coordinates except in AM1n for which the alignment is based on all atomic coordinates. See caption of Fig. S3 for conventions.
(A) MP2

(C) PM3n

(E) OM2n

(B) AM1n

(D) OM1n

(F) OM3n


Figure S6: Optimized water pentamer

Superimposition of the optimized geometries of the water pentamer (Entry (j) in Fig. 1). The alignment is based on all atomic coordinates. See caption of Fig. S3 for conventions.


## Figure S7: Gas-phase energy profiles for proton transfer: AM1 and AM1n

Comparison of MP2 (solid line), AM1 (dashed lines), and AM1n (dashed-dotted lines) gas-phase energy profiles for proton transfer between two water molecules in the Zundel ion for given oxygen-oxygen distances ( $R_{\mathrm{OO}}$ in $\AA$ ). Here, $\mathrm{d} r$ is the difference in the distances between the migrating proton and the two oxygen atoms. The MP2/aug-cc-pVTZ data obtained from relaxed surface scans in panel (A) were included in the training set, and those in panel (B) in the validation set. The AM1 curve is right beneath the AM1n curve.


Figure S8: Gas-phase energy profiles for proton transfer: PM3 and PM3n

Comparison of MP2 (solid line), PM3 (dashed lines), and PM3n (dashed-dotted lines) gas-phase energy profiles for proton transfer between two water molecules in the Zundel ion for given oxygen-oxygen distances ( $R_{\mathrm{OO}}$ in $\AA$ ). See caption of Fig. S7 for conventions.


## Figure S9: Gas-phase energy profiles for proton transfer: OM1 and OM1n

Comparison of MP2 (solid line), OM1 (dashed lines), and OM1n (dashed-dotted lines) gas-phase energy profiles for proton transfer between two water molecules in the Zundel ion for given oxygen-oxygen distances ( $R_{\text {OO }}$ in $\AA$ ). See caption of Fig. S7 for conventions. The OM1 curve is right beneath the OM1n curve.


## Figure S10: Gas-phase energy profiles for proton transfer: OM2 and OM2n

Comparison of MP2 (solid line), OM2 (dashed lines), and OM2n (dashed-dotted lines) gas-phase energy profiles for proton transfer between two water molecules in the Zundel ion for given oxygen-oxygen distances ( $R_{\mathrm{OO}}$ in $\AA$ ). See caption of Fig. S7 for conventions.


## Figure S11: Gas-phase energy profiles for proton transfer: OM3 and OM3n

Comparison of MP2 (solid line), OM3 (dashed lines), and OM3n (dashed-dotted lines) gas-phase energy profiles for proton transfer between two water molecules in the Zundel ion for given oxygen-oxygen distances ( $R_{\mathrm{OO}}$ in $\AA$ ). See caption of Fig. S7 for conventions.


## Figure S12: Water dimer geometries from relaxed surface scans

Water dimer geometries obtained in relaxed surface scans at the MP2/aug-cc-pVTZ level for (A) long $\left(R_{\mathrm{O} 1 \mathrm{O} 2} \geq 2.6 \AA\right)$ and $(\mathrm{B})$ short $\left(R_{\mathrm{O} 1 \mathrm{O} 2} \leq 2.5 \AA\right)$ distances between the oxygen atoms. Different relative orientations were observed: (A) the H11-O1-H12 plane bisects the angle $\mathrm{H} 21-$ $\mathrm{O} 2-\mathrm{H} 22$ with dihedral angle $\mathrm{H} 11-\mathrm{O} 1-\mathrm{H} 12-\mathrm{O} 2 \sim 0^{\circ}$; (B) both water molecules are in the same plane with dihedral angle $\mathrm{H} 11-\mathrm{H} 12-\mathrm{H} 21-\mathrm{H} 22 \sim 0^{\circ}$.


## Figure S13: Distributions of the sampled geometries

Distributions of the sampled geometries as functions of (A) the distance $R_{\text {O001' }}$ between the hydronium oxygen O 0 and the nearest potential acceptor $\mathrm{Ol}^{\prime}$; ( B ) the distance difference $\mathrm{d} r=\left|R_{\mathrm{OOH}^{\prime}}-R_{\mathrm{Ol}^{\prime} \mathrm{H}^{\prime}}\right|$, where $\mathrm{H}^{\prime}$ denotes the hydrogen atom between O 0 and $\mathrm{O1}^{\prime}$, and $R_{\mathrm{OOH}^{\prime}}\left(R_{\mathrm{Ol}^{\prime} \mathrm{H}^{\prime}}\right)$ are the distances between $\mathrm{O} 0\left(\mathrm{O}^{\prime}\right)$ and $\mathrm{H}^{\prime}$; and (C) the ratio $\rho$ (see Fig. 4 for definition).


## Figure S14: $\boldsymbol{R}_{0001}$ and $\boldsymbol{R}_{0001}$ at donor-acceptor swaps

Comparison of $R_{\mathrm{O} 0 \mathrm{O} 1}$ and $R_{\mathrm{O} 001^{\prime}}$ when the donor and acceptor atoms swap, from (A) PM3n, (B) OM1n, and (C) OM3n simulations. Here, $R_{\mathrm{O} 0 \mathrm{O} 1}\left(R_{\mathrm{OOO} 1^{\prime}}\right)$ is the distance between the donor O0 and the acceptor O 1 (the nearest potential acceptor $\mathrm{O} 1^{\prime}$ ). Usually O 1 and $\mathrm{O} 1^{\prime}$ are identical at the time of swapping: O1' differs from O1 only in $1.6 \%$ of the swaps (5 out of 305) for PM3n, in $0.5 \%$ ( 50 out of 9364 ) for OM1n, and 2.7\% (128 out of 4678) for OM3n.


Figure S15: Distribution of $R_{0001}$ at donor-acceptor swaps

Distribution of the donor-acceptor distance $R_{\mathrm{O} 001}$ at the moment when the donor and acceptor swap. The average $R_{\text {O0O1 }}$ values are $2.37 \AA, 2.33 \AA$, and $2.41 \AA$ for PM3n, OM1n, and OM3n, respectively.


## Figure S16: Integrated coordination number $\boldsymbol{n}_{\mathrm{OO}}(r)$ of water

Integrated coordination number $n_{\mathrm{OO}}(r)$ for bulk water by the (A) SPC and TIP3P water models, (B) MNDO-based AM1 and PM3 models, and (C) orthogonalization-corrected OM1 and OM3 models. Results are shown for the authentic and the re-parameterized semi-empirical methods.


## Figure S17: Integrated coordination number $n_{\mathrm{OH}}(r)$ of water

Integrated coordination number $n_{\mathrm{OH}}(r)$ for bulk water by the (A) SPC and TIP3P water models, (B) MNDO-based AM1 and PM3 models, and (C) orthogonalization-corrected OM1 and OM3 models. Results are shown for the authentic and the re-parameterized semi-empirical methods.


Figure S18: Integrated coordination numbers $n_{\mathrm{OOO}}(r)$ and $n_{\mathrm{OOH}}(r)$ of solvated proton

Integrated coordination numbers $(\mathrm{A}) n_{\mathrm{OOO}}(r)$ and (B) $n_{\mathrm{OOH}}(r)$ for solvated proton obtained from the re-parameterized semi-empirical methods.



