Quantum Monte Carlo study of protonated water dimer

A simple model of proton transfer in water

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28/11/2013

Contents

Proton transfer in water

Proton transfer in water and aqueous systems is an ubiquitous phenomenon ⇒ relevant in a wide range of fields:

- basic mechanism of charge transfer in cells membranes
- important role in several enzymathic reactions
- design and application of efficient fuel cells

Despite its importance a **detailed and quantitative explanation** of the proton transfer (PT) mechanism has not been found yet.

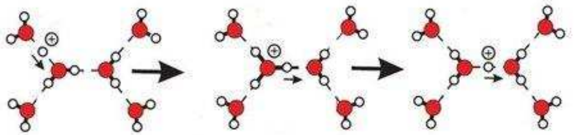

Figure: Proton transfer in water.

Proton transfer in water

- Molecular dynamics simulations based on *ab-initio* potential energy surfaces (PESs) have not reached an agreement with experimental results. Due to:
  - Accurate description of hydrogen bonds formation, stretching and breaking is compulsory.
  - Sensitive thermal behavior ⇒
    ⇒ Precision of the order of 0.1 Kcal/mol is required by the PESs.

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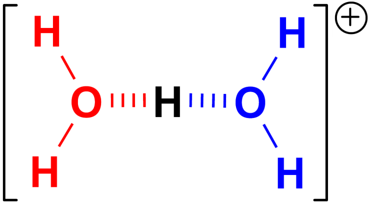
$$\Downarrow$$

- Precision reached by recent **highly correlated methods** such as coupled cluster (CC) technique.
- Accurate results for small systems, but simulations of larger protonated clusters is *in general* not feasible.

$H_5O_2^+$ or **Zundel ion** represents the simplest model of PT in water ⇒ subject of many experimental and theoretical investigations.



Subject: extensive study of this model the by means of several **quantum Monte Carlo** (QMC) techniques:

- **favorable scaling** $\sim N^3$ ⇒ simulation of larger protonated water clusters.
- **global accuracy** close to state-of-the-art CCSD(T) technique for both energetics and geometry.

Goal: work out and test a PES of Zundel ion which pave the way for further QMC computations on more realistic PT models.

Contents

Wave function ansatz: JAGP

QMC ansatz is the product of two factors: bosonic **Jastrow** factor and fermionic **Antisymmetrised Geminal Power** (AGP) function.

$$\Psi(\mathbf{x_1}, ..., \mathbf{x_n}) = J(\mathbf{r_1}, ..., \mathbf{r_n})\Psi_{\mathrm{AGP}}(\mathbf{x_1}, ..., \mathbf{x_n}) \tag{1}$$

where $\{\mathbf{x_i} = (\mathbf{r_i}, \sigma_i)\}$ are the coordinates of electron i.

Basis set

We employ a primitive Gaussian basis set:

$$\psi^{\mathrm{GTO}}_{a,(l,m,n)}(\mathbf{r}) = |\mathbf{r} - \mathbf{R}_a|^l e^{-\zeta_{l,n}|\mathbf{r}-\mathbf{R}_a|^2} Z_{l,m}(\Omega_{\mathbf{r}-\mathbf{R}_a}) \tag{2}$$

$Z_{l,m}(\Omega)$ = spherical harmonics , $\{l, m\}$ = quantum numbers, n = gaussian index, ζ = gaussian exponents

Jastrow factor

It treats dynamical correlations associated charge fluctuations → *Van der Waals forces*. Main contribution is represented by the **three/four body term** which takes into account electron-electron-ion interactions:

$$J_3(\mathbf{r}_1, ..., \mathbf{r}_N) = \exp\left(\sum_{i<j} \Phi_J(\mathbf{r}_i, \mathbf{r}_j)\right) \quad (3)$$

$$\Phi_J(\mathbf{r}_i, \mathbf{r}_j) = \sum_{a,b}^{N_{\mathrm{atoms}}} \sum_{\mu,\nu}^{N_{\mathrm{basis}}} g_{\mu,\nu}^{a,b} \psi_{a,\mu}^{\mathrm{GTO}}(\mathbf{r}_i) \psi_{b,\nu}^{\mathrm{GTO}}(\mathbf{r}_j) \quad (4)$$

where $\mu, \nu = \{l, m, n\}$, N_{atoms} = number of atoms, N_{basis} = total number of GTOs

AGP function

It accounts for static correlations associated to nearly-degenerated electronic energy levels.

- Antisymmetric product of pairing functions or geminals $\Phi(\mathbf{x}_i, \mathbf{x}_j)$ of the system.

$$\begin{aligned} \Psi_{\rm AGP}(\mathbf{x}_1, \ldots, \mathbf{x}_n) &= \hat{\rm A}\left[\Phi(\mathbf{x}_1, \mathbf{x}_2), \ldots \Phi(\mathbf{x}_{N-1}, \mathbf{x}_N)\right] && (5) \\ \Phi(\mathbf{x}_i, \mathbf{x}_j) &= \phi(\mathbf{r}_i, \mathbf{r}_j)\frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right) && (6) \end{aligned}$$

- So far geminals have been expanded over the uncontracted basis set:

$$\phi(\mathbf{r}_i, \mathbf{r}_j) = \sum_{a,b}^{N_{\rm atoms}} \sum_{\mu,\nu}^{N_{\rm basis}} \lambda_{a,b}^{\mu,\nu} \psi_{a,\mu}^{\rm GTO}(\mathbf{r}_i) \psi_{b,\nu}^{\rm GTO}(\mathbf{r}_j) \tag{7}$$

where $\mu, \nu = \{l, m, n\}$, $N_{\rm atoms}$ = number of atoms, $N_{\rm basis}$ = total number of GTOs

Atomic hybrid orbitals

Set of hybrid orbitals for each atom = contraction of primitive basis which maintains atomic character:

$$
\begin{aligned}
\phi(\mathbf{r}_i, \mathbf{r}_j) &= \sum_{a,b}^{N_{\text{atoms}}} \sum_{\alpha,\beta}^{N_{\text{hyb}}} \tilde{\lambda}^{a,b}_{\alpha,\beta} \psi^{\text{hyb}}_{a,\alpha}(\mathbf{r}_i) \psi^{\text{hyb}}_{b,\beta}(\mathbf{r}_j) & (8) \\
\psi^{\text{hyb}}_{a,\alpha}(\mathbf{r}) &= \sum_{\mu} c^{\alpha}_{\mu} \psi^{\text{GTO}}_{a,\mu}(\mathbf{r}) & (9)
\end{aligned}
$$

where $\mu = \{l, m, n\}$, N_{hyb} = number of hybrids for each atom.

- Information in local electronic structure *and* nuclear embedding in the compound.
- energy loss $\leq$ 1 mH with respect to uncontracted expansion
- number of parameters with hybrids $P^{\text{hyb}} \propto N^2_{\text{hyb}}$ vs $P^{\text{uncontr}} \propto N^2_{\text{basis}}$ of the uncontracted expansion ⇒ decreased of a factor 2 which becomes larger when system size is increased.

Computational details

Wave function optimization

Robust optimization of the wave function:

1. Ansatz is generated at first at a density function theory level.
2. Variational Monte Carlo technique is then applied to optimize the variational parameters of the ansatz all together.

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Energy computations

Energy calculations are carried out with both **Variational Monte Carlo (VMC)** and **Diffusion Monte Carlo (DMC)** schemes. *BFD Pseudopotentials* are employed to treat oxygen core electrons.

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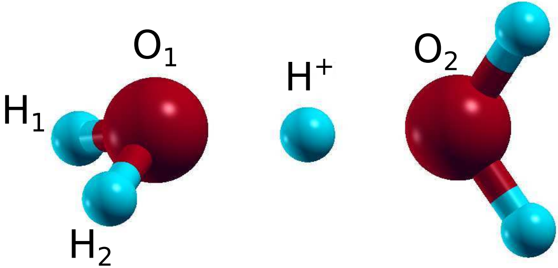
Geometry computations

1. QMC estimators allows computation of **atomic forces** as efficiently as total energy calculations.
2. **Structure relaxation** is performed at VMC level of theory

Contents

Ground state geometry

Figure: C_2-sym global minimun of Zundel ion. Main geometrical parameters (distances are in Å and angles in °) are shown in the table at the bottom. Agreement between QMC and CC is up to 0.005 Å for separations and 1° for the angle.



Method	$d(O_1O_2)$	$d(O_1H^+)$	$d(O_2H^+)$	$\angle O_1H^+O_2$	$d(O_1H_1)$	$d(O_1H_2)$
DFT-PBE	2.4111	1.2074	1.2074	173.684	0.9697	0.9691
QMC	2.3847(5)	1.1930(5)	1.1942(8)	174.71(7)	0.9605(8)	0.9650(8)
CCSD(T)	2.3864	1.1950	1.1950	173.730	0.9686	0.9682

Proton Transfer in the $H_5O_2^+$

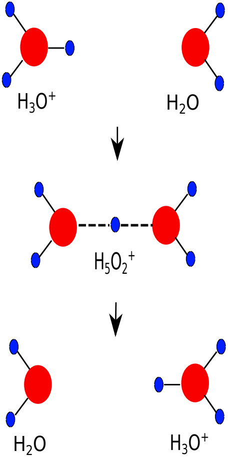
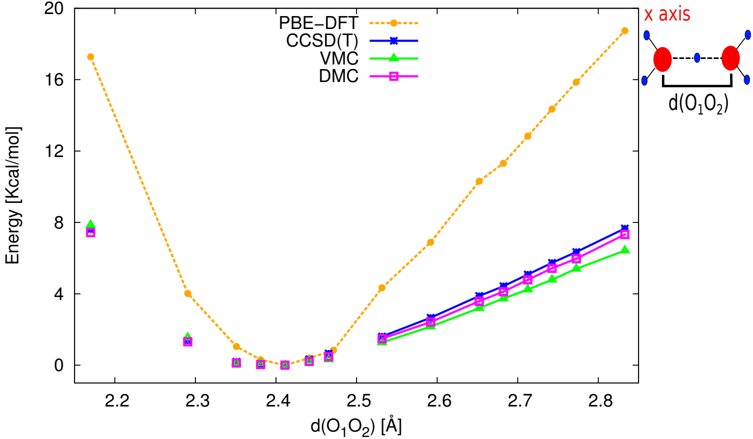


Figure: Proposed general mechanism of proton transfer ⇒ guideline to choose the reaction coordinate for the potential energy curve.

Potential energy curve

Figure: Potential energy curve of the dimer as a function of the oxygen-oxygen distance. QMC-optimized geometry is employed for every technique. **CCSD(T)** results are obtained from the full dimensional PES by Huang *et al.* [1]



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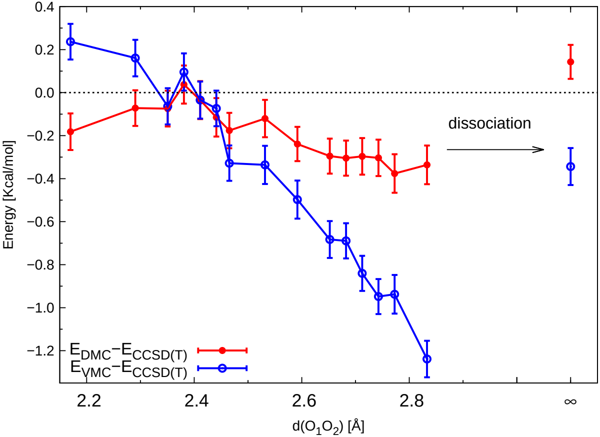
[1] X. Huang, B. J. Braams, J. M. Bowman, J. Chem. Phys. **122**, 044308 (2005)

Potential energy curve

Figure: Potential energy curve of the dimer at different level of theory with respect to coupled cluster energies (zero of the axis).



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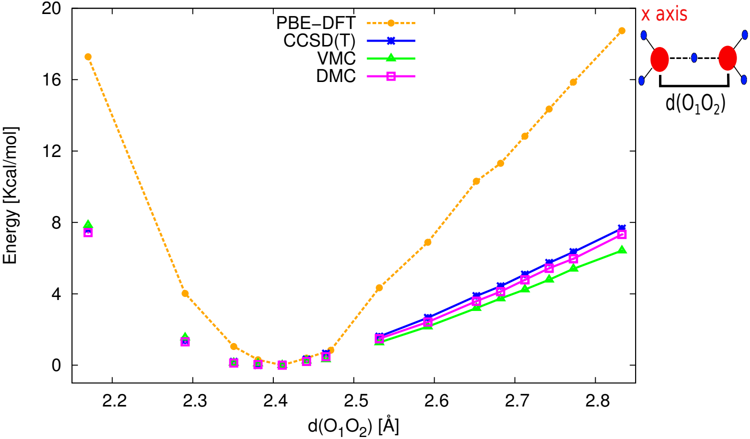

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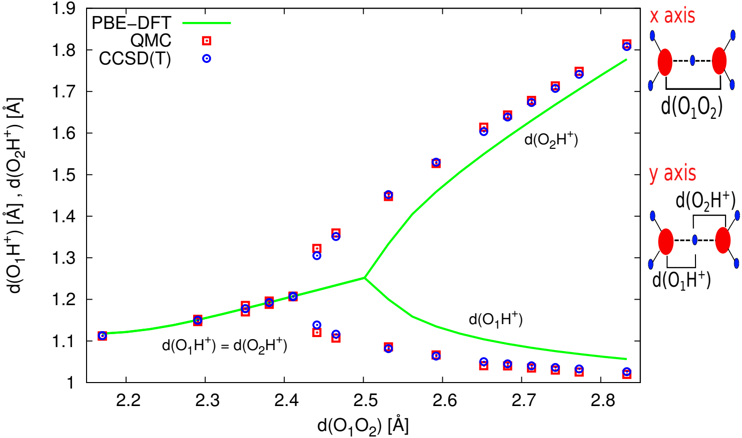
Excess proton behavior

Figure: Geometrical properties of the excess proton along the reaction coordinates at different level of theory.



Proton transfer static barrier

Figure: Proton transfer static barrier (Kcal/mol) in the Zundel model. It is computed as difference between the two displayed configurations at different $\overline{OO}$ distances.

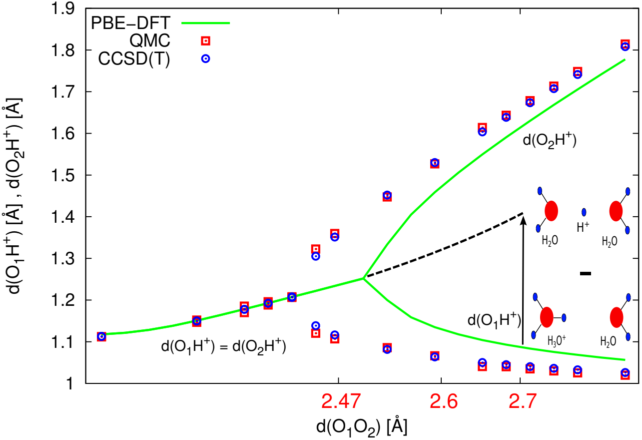


Table: Values of proton transfer barriers (Kcal/mol) at different $\overline{OO}$ separations. The first column values are computed at distance very close to the symmetry-breaking point where the barrier is very tiny, slightly above the QMC statistical error.

Method	d($O_1 O_2$)		
	2.47 Å	2.6 Å	2.7 Å
DFT-PBE	-0.74	0.19	1.94
VMC	0.28(6)	2.99(8)	5.99(8)
DMC	0.37(8)	2.64(7)	5.57(7)
CCSD(T)	0.28	2.29	5.32

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Conclusions

What has been done

- $H_5O_2^+$, simplest model of proton transfer in water, has been investigated by means of several QMC techniques.
- energetics in excellent agreement with CCSD(T) results, up to 0.3 Kcal/mol for DMC, up to 1 Kcal/mol for VMC.
- VMC structural relaxation provides geometries remarkably close to CCSD(T).
- Key role of correlations to describe proton transfer physics in the system ⇒ important in more realistic models.

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Future directions

- Studies of more realistic models allowed by QMC favorable scaling.
- Introduction of finite temperature within QMC framework.
- Introduction of the quantum nature of protons.

Thank you for your attention!

Atomic hybrid orbitals

Basis set

Jastrow: O(3s2p1d)H(2s1p)
AGP: O(5s5p2d)H(4s2p)

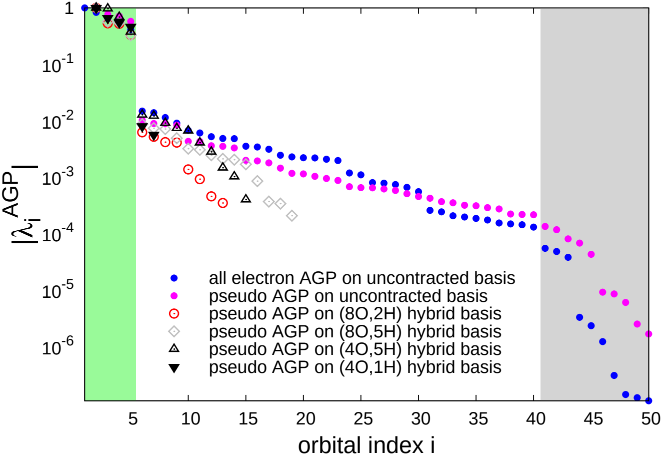
Best set of hybrids

- Variational parameters: $P_{\mathrm{hyb}} = N^2_{\mathrm{total\ hyb}} + N_{\mathrm{basis}} \times N_{\mathrm{total\ hyb}}$
- Benchmark Variational Monte Carlo (VMC) pseudopotential calculations on a single water molecule.
- Assess the best compromise between efficiency (number of parameters) and accuracy (variational energy) for atomic hybrid basis.

Wave function ansatz	VMC energies		number of parameters		
	Energy E (H)	ΔE (mH)	$\lambda^{a,b}_{\alpha,\beta}$	det orbitals	total
JAGP (uncontracted orbitals)	-17.25389(6)	0.0	682	18	895
JAGP (hybrid orbitals: 8O 5H)	-17.25302(6)	0.87(8)	171	358	724
JAGP (hybrid orbitals: 8O 2H)	-17.25267(7)	1.22(9)	78	298	571
JAGP (hybrid orbitals: 4O 5H)	-17.25183(6)	2.06(8)	105	238	538
JAGP (hybrid orbitals: 4O 1H)	-17.25013(8)	3.7(1)	21	158	374

Why AGP ansatz?

Figure: Modulus of the AGP eigenvalues λ_i as a function of the molecular orbital index. Calculations done for a single H_2O molecule.



Why JAGP ansatz?

Table: Pseudopotential calculations on single H_2O molecule. Test of various wave function ansatzes.

Wave function ansatz	VMC energies		
	Energy E_x (H)	Variance (H^2)	$E_x - E_{\mathrm{JSD}}$ (mH)
JSD (uncontracted)	-17.24821(7)	0.2655(6)	0.0
JAGP (hybrid: 4O 1H)	-17.25013(8)	0.2635(12)	-1.91(11)
JAGP (hybrid: 4O 5H)	-17.25183(6)	0.2510(6)	-3.62(10)
JAGP (hybrid: 8O 2H)	-17.25267(7)	0.2426(18)	-4.46(10)
JAGP (hybrid: 8O 5H)	-17.25302(6)	0.2412(34)	-4.89(10)
JAGP (uncontracted)	-17.25389(6)	0.2296(5)	-5.68(10)

Table: DMC energy results on H_2O. JAPG provides a better description of the nodal surface of the wave function.

	pseudo	all-electron
E_{JSD} (H)	-17.26280(6)	-76.42475(15)
E_{JAGP} (H)	-17.26528(6)	-76.42690(14)
$E_{\mathrm{JAGP}-E_{\mathrm{JSD}}}$ (mH)	-2.48(9)	-2.15(21)

More realistic model of PT in water

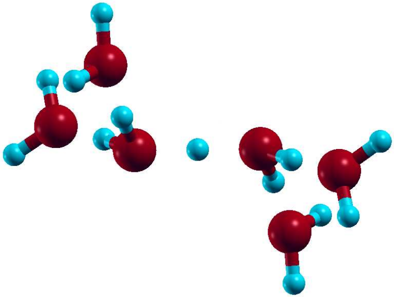


Figure: In table below: computational time for single-point energy calculations for various clusters sizes.

	Total wall time (h) on 512 CPU	
# of water molecules	VMC	LRDMC
1	0.05	0.15
2	0.24	2.13
6	6.18	49.58