
QMC dissociation energy of the water dimer: Time step errors and backflow calculations

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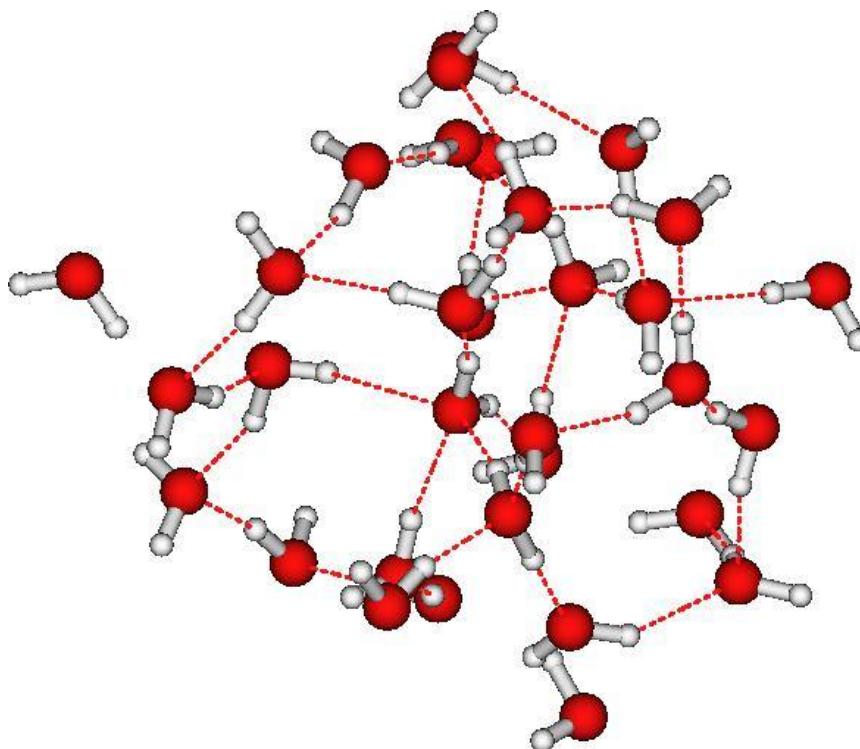
University of Cambridge



Introduction

■ Water

Physical and chemical properties: strong polar hydrogen bonds



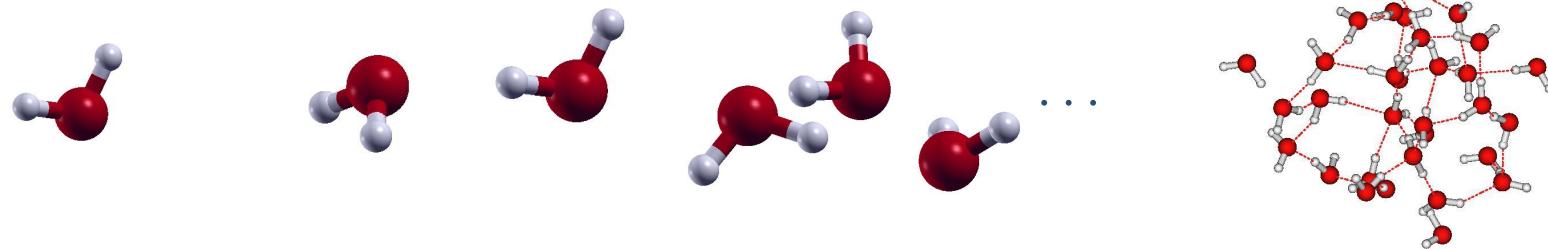
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Introduction

■ Water

Physical and chemical properties: strong polar hydrogen bonds

■ Monomer → Dimer → Trimer → ... → Bulk water



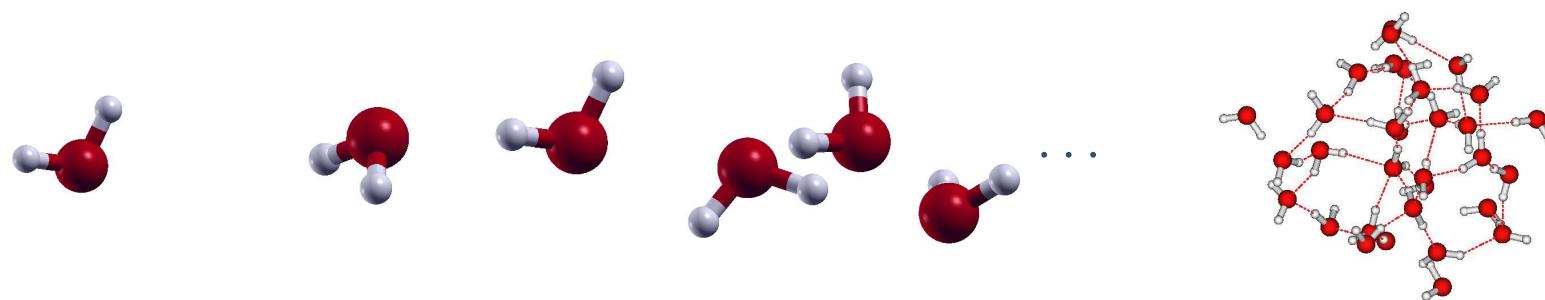
Binding energy of only a few kcal/mol

Introduction

■ Water

Physical and chemical properties: strong polar hydrogen bonds

■ Monomer → Dimer → Trimer → ... → Bulk water



Binding energy of only a few kcal/mol

■ DIMER: prototype of all hydrogen-bonded systems

Previous calculations on H₂O and (H₂O)₂

- MP2, CCSD(T), CI
 - + correlation effects quite accurate
 - basis set truncation errors
 - basis set superposition errors
 - N^5, N^7

Previous calculations on H₂O and (H₂O)₂

■ MP2, CCSD(T), CI

- + correlation effects quite accurate
- basis set truncation errors
- basis set superposition errors
- N^5, N^7

■ Density functional theory (DFT)

- + More favorable scaling
- Strong dependence on the XC functional

This work on H₂O and (H₂O)₂

■ Quantum Monte Carlo

- + electronic correlation explicitly
- + Scales as N^3

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This work on H₂O and (H₂O)₂

■ Quantum Monte Carlo

- + electronic correlation explicitly
- + Scales as N^3

THIS WORK

- ⇒ VMC and DMC Energies of H₂O and (H₂O)₂
 - ◆ All-electron (AE) and Pseudopotential (PP) calculations
 - ◆ Slater-Jastrow (SJ) and Slater-Jastrow-Backflow (BF) wave functions
- ⇒ Electronic dissociation energy of (H₂O)₂

VMC, DMC

■ VMC

- ◆ Accuracy determined by the trial wave function
- ◆ biased energy differences
- ◆ for optimizing parameters of the wave function

■ DMC

- ◆ Project out the ground state component of the trial wave function
- ◆ Fermionic symmetry: fixed node approximation

CASINO code

Trial wave function

■ Slater-Jastrow (SJ) wave function

$$\Psi^{\text{SJ}}(\mathbf{R}) = e^{J(\mathbf{R})} \Psi_S(\mathbf{R})$$

- ◆ $\mathbf{R}=\{\mathbf{r}_i\}$
- ◆ Jastrow factor: $e^{J(\mathbf{R})}$
- ◆ Slater determinant: $\Psi_S = D_\uparrow D_\downarrow$

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■ Slater-Jastrow-Backflow (BF) wave function

$$\Psi^{\text{BF}}(\mathbf{X}) = e^{J(\mathbf{R})} \Psi_{\text{S}}(\mathbf{X})$$

$$\mathbf{x}_i = \mathbf{r}_i + \xi_i(\mathbf{R})$$

- ◆ Backflow displacement: $\xi_i(\mathbf{R})$ [PLR: 24/07, 9:30am]

Single particle orbitals

- CRYSTAL98 code
- Basis set: Roos augmented double zeta ANO (s, p, d)
- B3LYP orbitals seem to give better nodes than Hartree-Fock orbitals
→ use parameters in XC functional to optimise orbitals

Single particle orbitals

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$$E_{\text{xc}} = (1 - A)(E_x^{\text{LDA}} + B E_x^{\text{Becke}}) + A E_x^{\text{HF}} + (1 - C) E_c^{\text{VWN}} + C E_c^{\text{LYP}}$$

- A : Fock exchange
- B : non-local exchange
- C : non-local correlation

True B3LYP → $A = 0.2$, $B = 0.9$ and $C = 0.81$

B3LYP orbitals

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$$E_{xc} = (1 - A)(E_x^{\text{LDA}} + B E_x^{\text{Becke}}) + A E_x^{\text{HF}} + (1 - C) E_c^{\text{VWN}} + C E_c^{\text{LYP}}$$

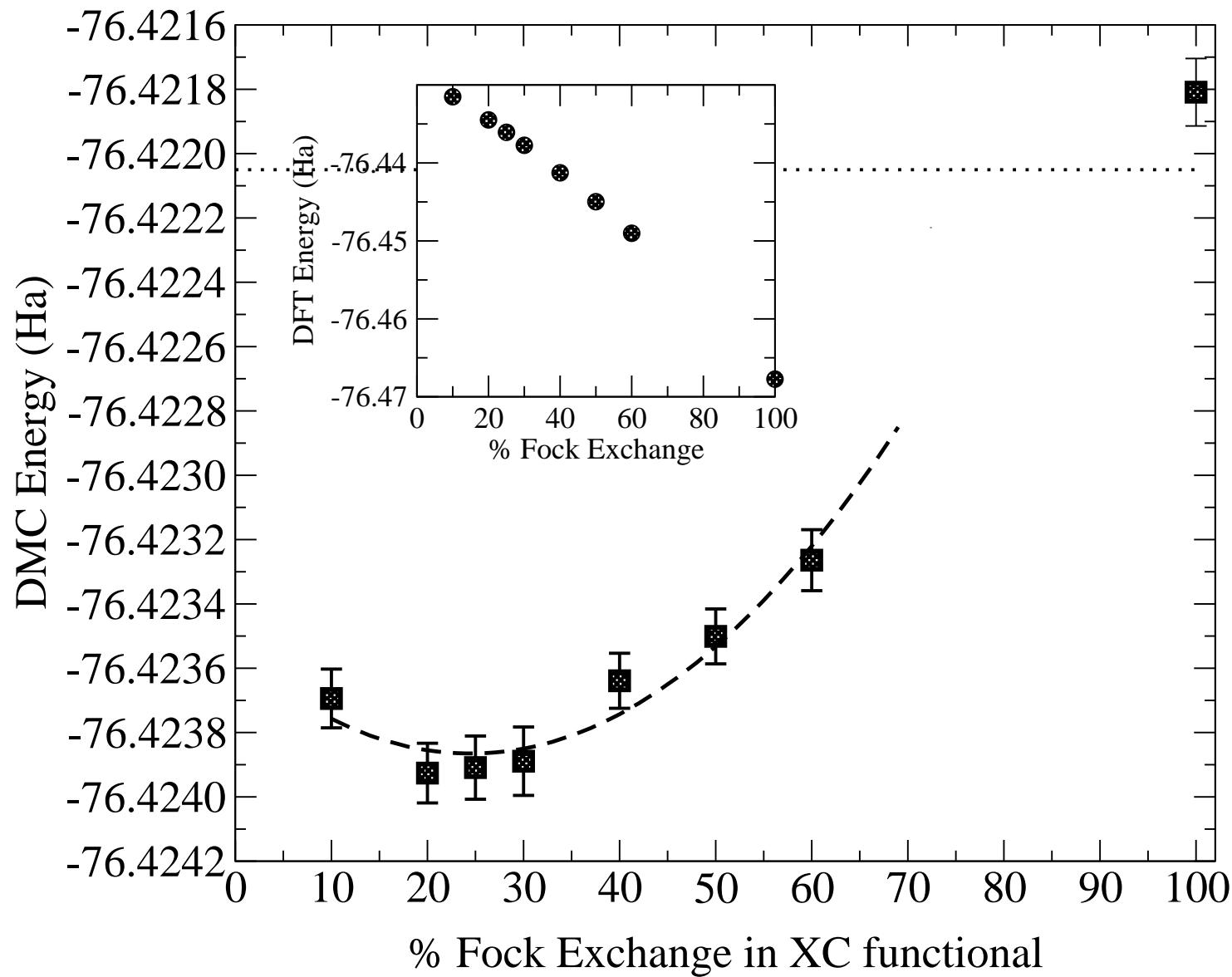
$$\begin{aligned} A = 1 &\implies E_{\text{DMC}} = -76.4218(1) \text{ Ha} \\ \text{HF} &\implies E_{\text{DMC}} = -76.42205(8) \text{ Ha} \end{aligned}$$

■ Exchange is the most important contribution

⇒ Use A as optimisable parameter keeping B and C constant

B3LYP-25 orbitals

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Summary of details

- SJ and BF trial wave functions
- J/BF parameters: minimize variance of local energy
- B3LYP-25 single-particle orbitals
- AE: single-particle orbitals corrected → obey cusp conditions
- PP: From Hartree-Fock theory
 - ◆ work well with QMC
 - ◆ avoid short-range variations of the wavefunction near the nuclei
 ⇒ larger time steps
- Various time steps + extrapolation to zero time

Geometries

■ Monomer: experimental equilibrium geometry



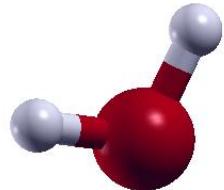
$$r_{\text{OH}} = r_{\text{OH}'} = 0.9572 \text{ \AA}$$
$$\angle = 104.52^\circ$$

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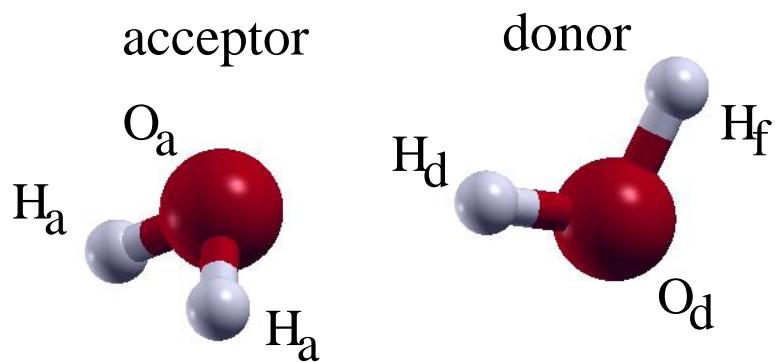
■ Monomer: experimental equilibrium geometry



$$r_{OH} = r_{OH'} = 0.9572 \text{ \AA}$$

$$\angle = 104.52^\circ$$

■ Dimer: CCSD(T) geometry (Klopper *et. al*)



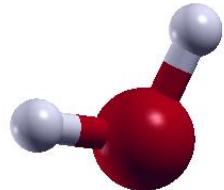
$$r_{\text{OO}} = 2.912 \text{ \AA}$$

(Deformations
neglected)

Geometries

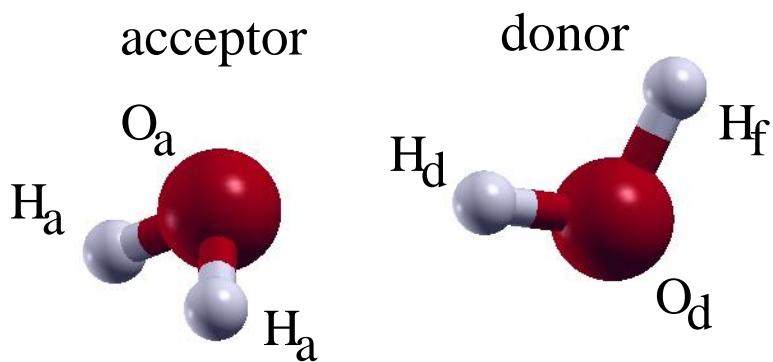
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$$r_{OH} = r_{OH'} = 0.9572 \text{ \AA}$$

■ Dimer: CCSD(T) geometry (Klopper *et. al*)



$$r_{\text{OO}} = 2.912 \text{ \AA}$$

(Deformations neglected)

■ Electronic dissociation energy



$$D_e = D_o - \text{ZPE}$$

Water monomer total energy (Ha)

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	B3LYP-like	-76.4361
	Exact	-76.438

Water monomer total energy (Ha)

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	VMC-SJ	-76.3773(2)
	DMC-SJ	-76.4230(1) -76.42371(6)
	B3LYP-like	-76.4361
	Exact	-76.438

Water monomer total energy (Ha)

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VMC-SJ

-76.3773(2)

— — — — —

DMC-SJ (HF)

-76.42102(4)

-76.4219(1)

-76.4230(1)

-76.42371(6)

— — — — —

B3LYP-like

-76.4361

Exact

-76.438

Water monomer total energy (Ha)

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	VMC-SJ	-76.3773(2)	84%
	VMC-BF	-76.4010(1)	90%
 	DMC-SJ DMC-BF	-76.42371(6) -76.42792(15)	96.2% 97.4%
	Exact	-76.438	

Water monomer total energy (Ha)

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	VMC-SJ	-76.3773(2)
	VMC-BF	-76.4010(1)
	DMC-SJ	-76.42371(6)
	DMC-BF	-76.42792(15)
	DMC-PNO-CI	-76.429(1)
	Exact	-76.438

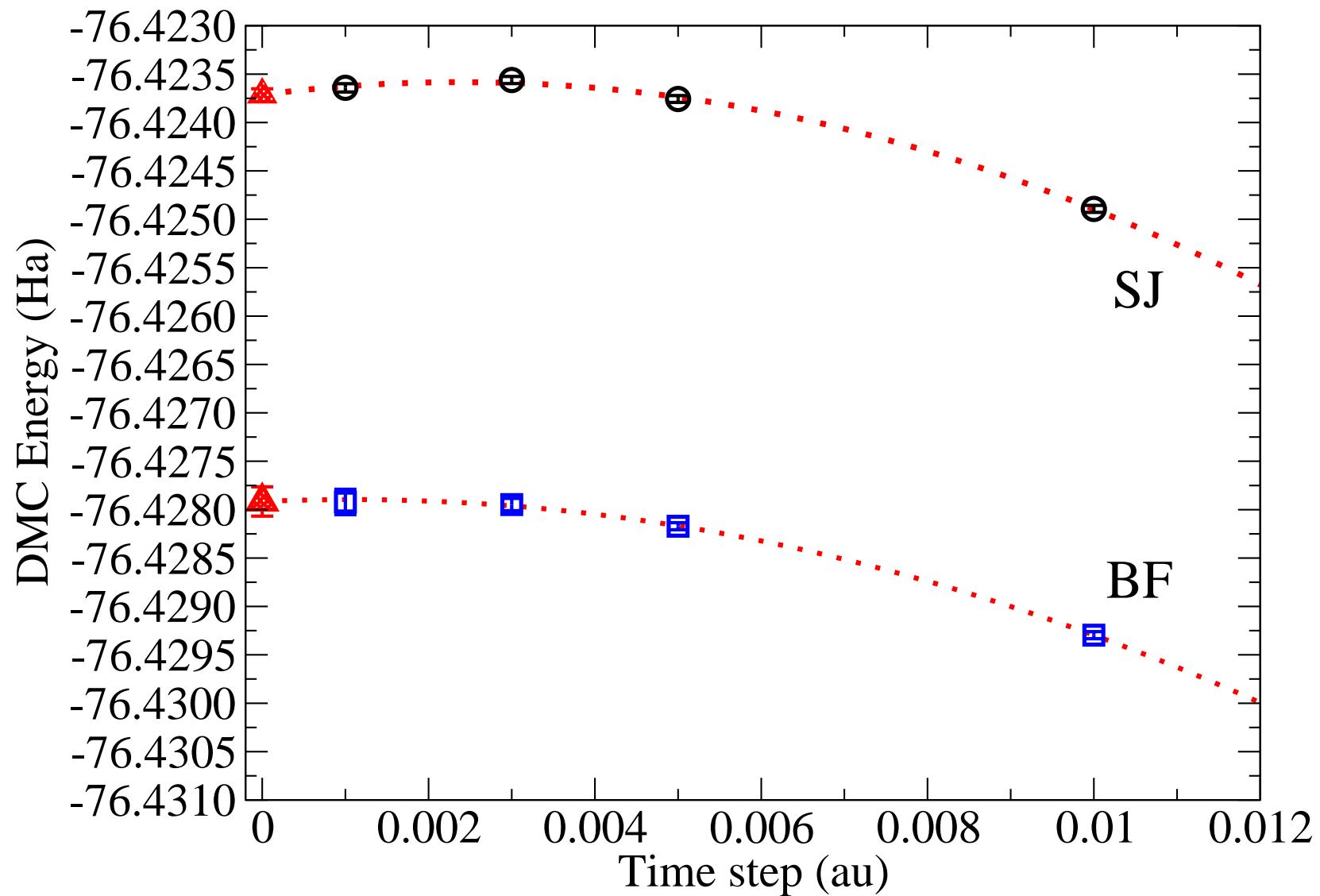
Water monomer total energy (Ha)

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	VMC-SJ	-76.3773(2)
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	DMC-BF	-76.42792(15)
	DMC-PNO-CI	-76.429(1)
	CCSD(T)-R12	-76.4373
	Exact	-76.438

H_2O , extrapolation to zero time

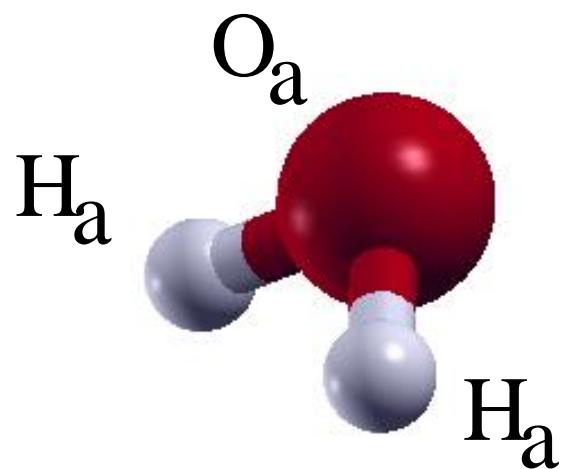
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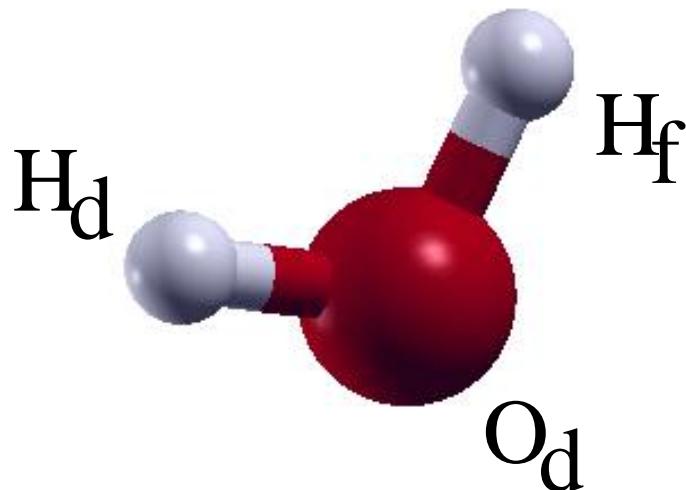
Water dimer

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acceptor

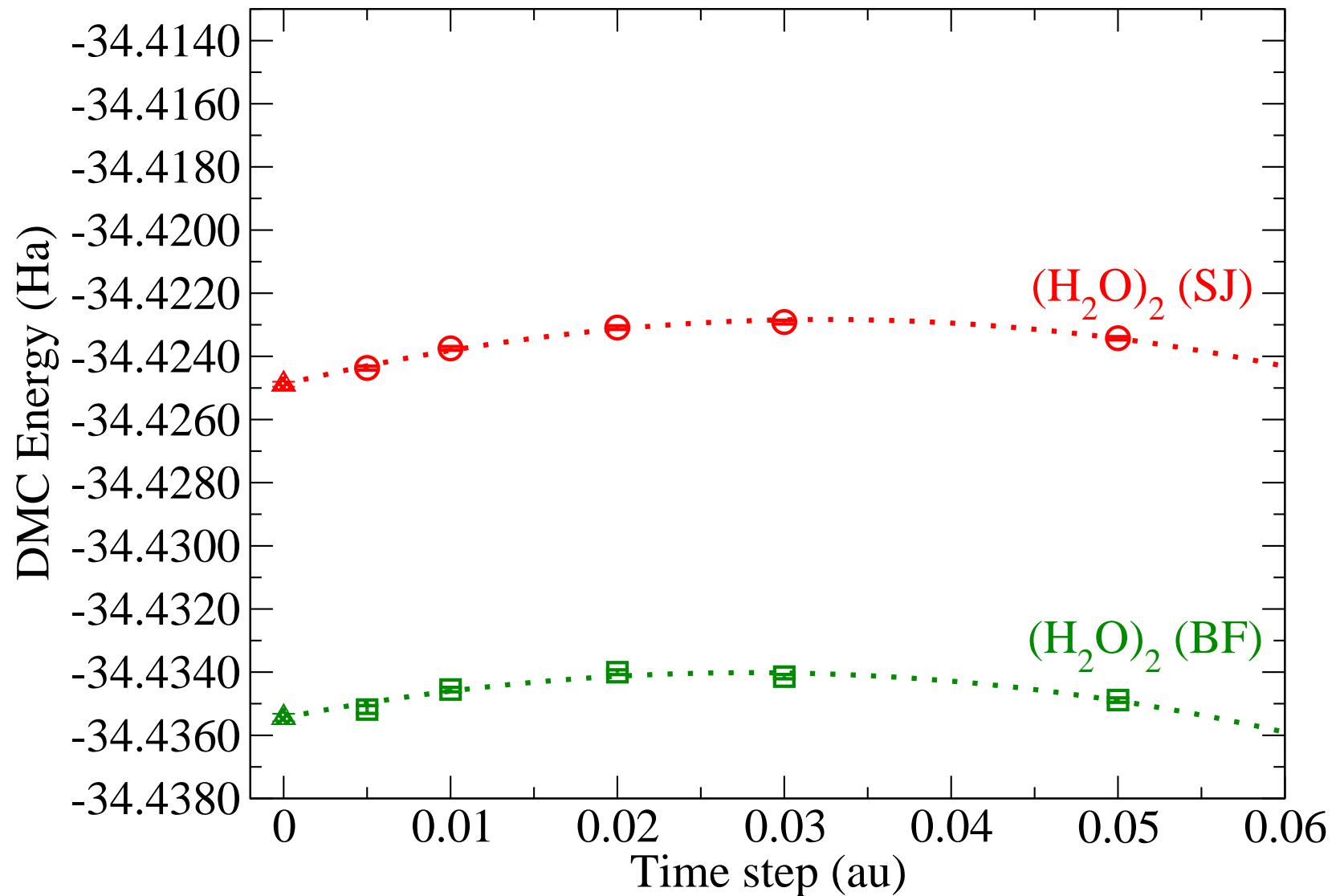


donor



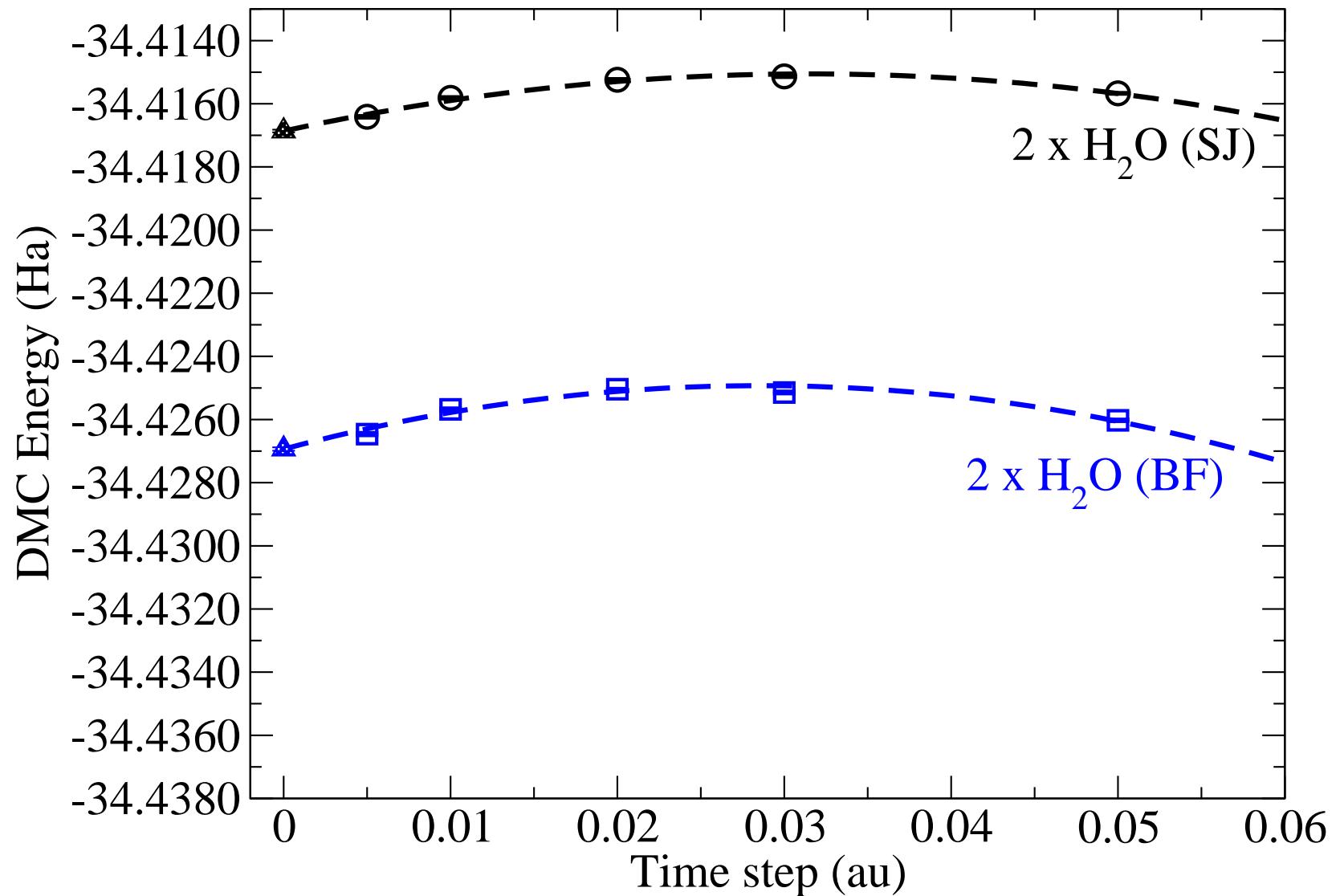
Pseudopotential calculations

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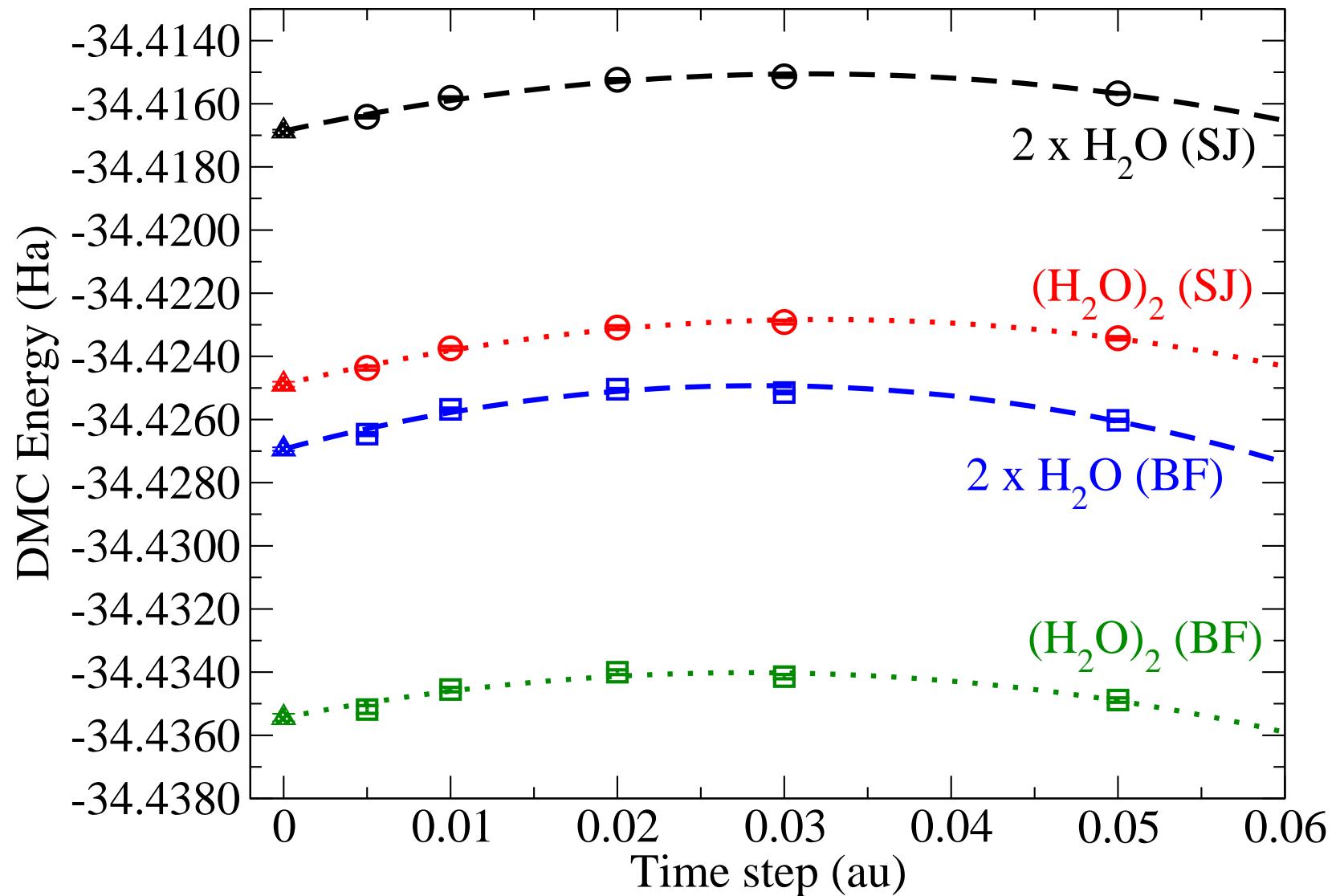
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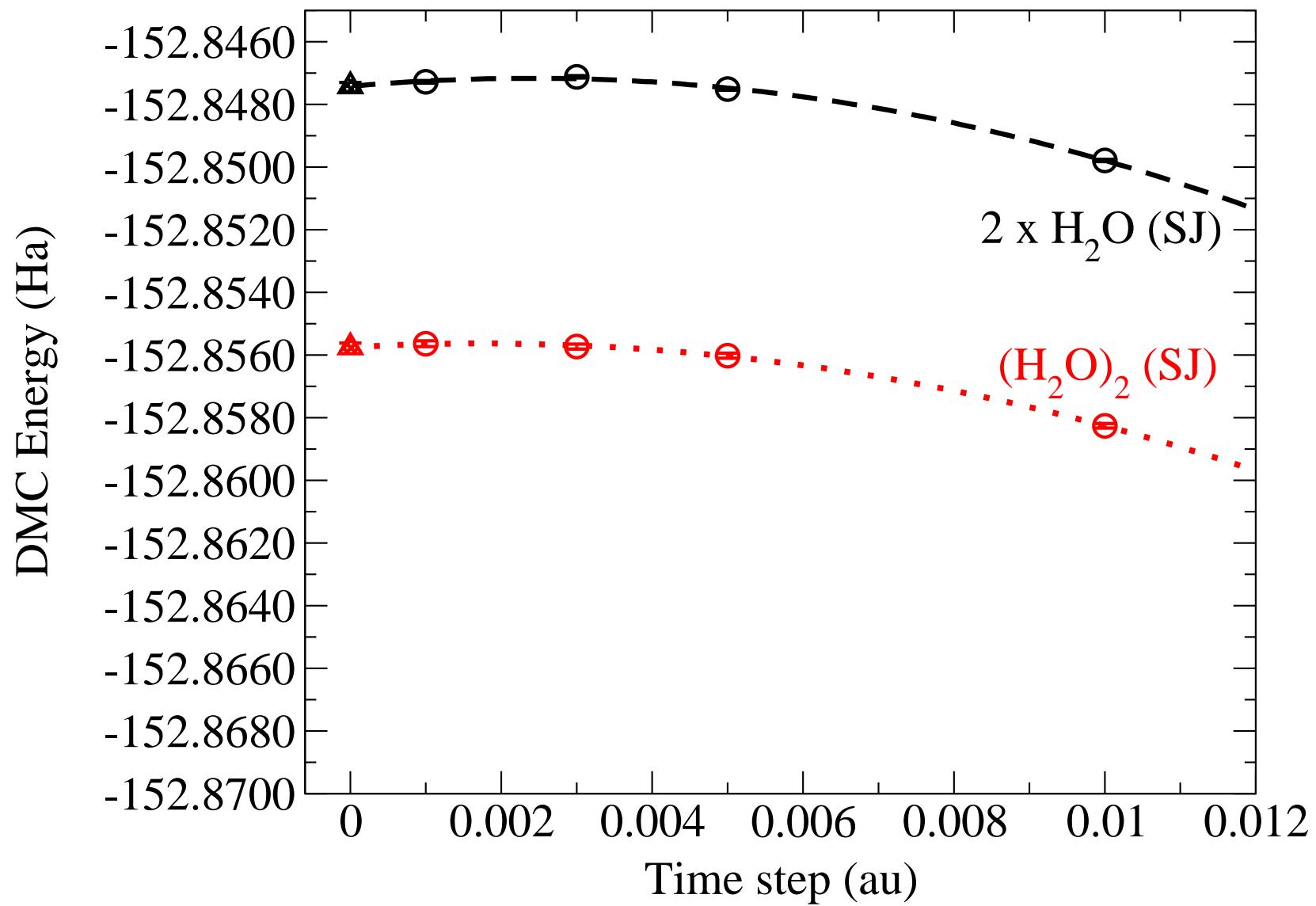
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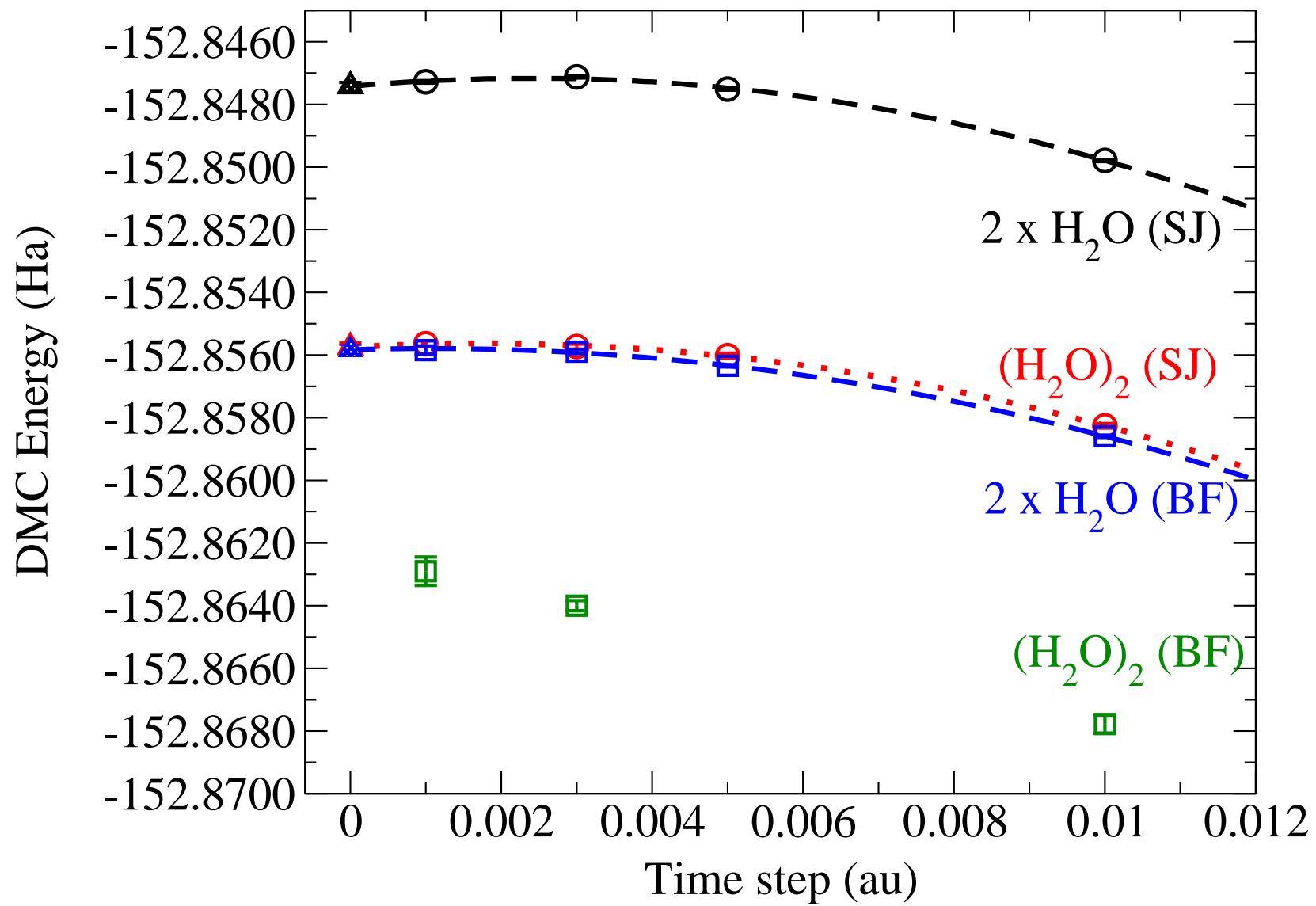
All-electron calculations

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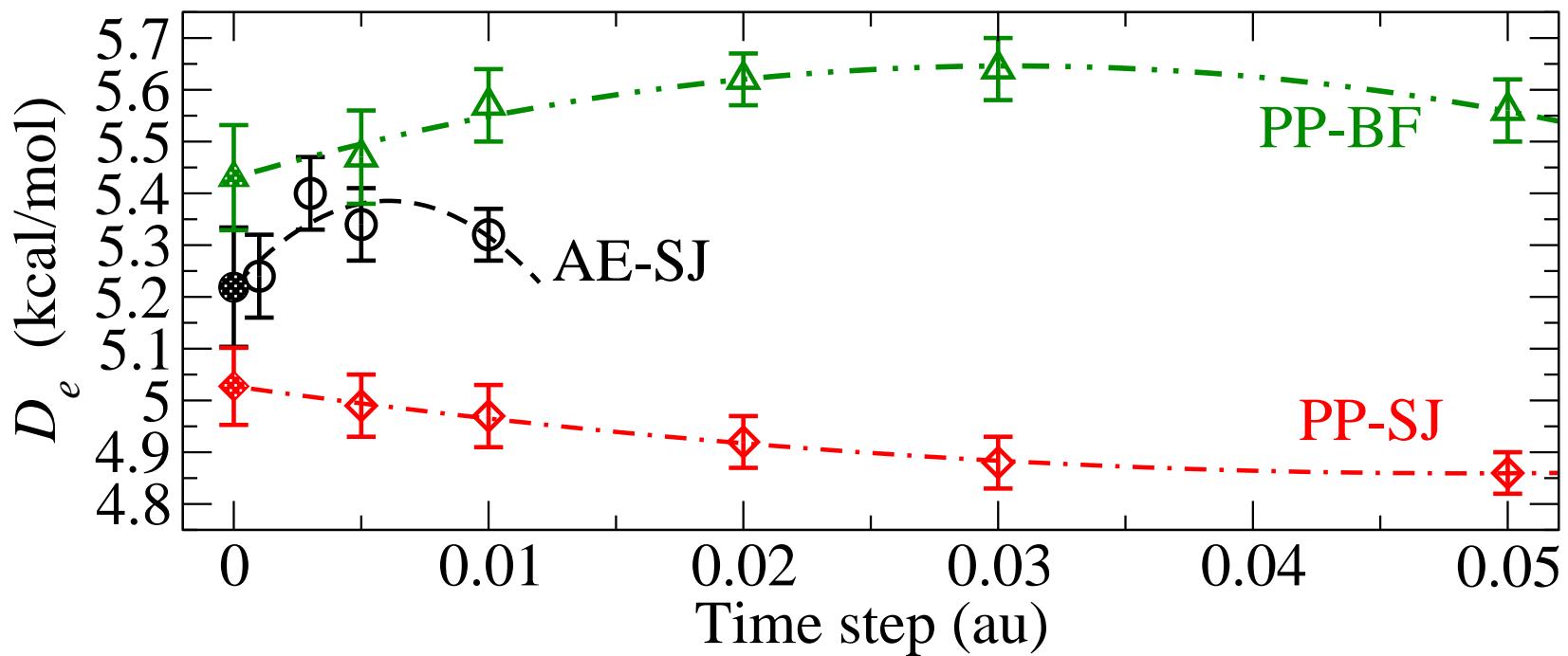
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Dissociation energy (D_e)

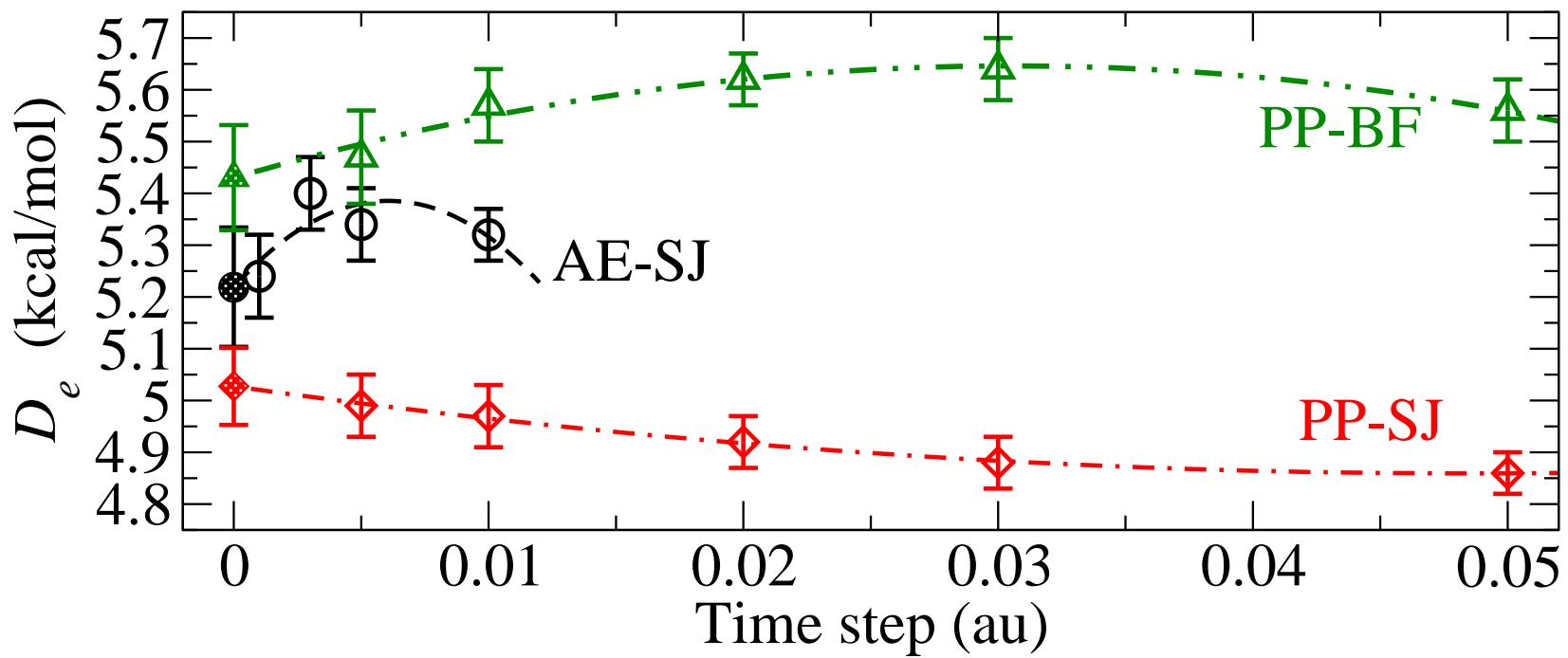
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Method	D_e (kcal/mol)
AE-SJ	5.23(11)
PP-SJ	5.03(7)
PP-BF	5.43(10)

Dissociation energy (D_e)

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Method	D_e (kcal/mol)
AE-SJ	5.23(11)
PP-SJ	5.03(7)
PP-BF	5.43(10)

DMC-HF	5.02(18)
DMC-B3LYP	5.21(18)
CCSD(T)	5.04(5)
Exp	5.44(70)
Exp	5.00(70)

Conclusions

- AE and PP total energies of H_2O and $(\text{H}_2\text{O})_2$
- SJ and BF wave functions with B3LYP-like single-particle orbitals

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Conclusions

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- Water monomer
 - ◆ B3LYP-like orbitals lower the H_2O DMC energy ~ 1.5 mHa compared to HF orbitals
→ better nodal surface
 - ◆ BF correlations reduce the DMC energy by an additional 4-5 mHa
 - ◆ $E = -76.42792(15)$ Ha (10 mHa above exact value)

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 - ◆ $E = -76.42792(15)$ Ha (10 mHa above exact value)
- D_e of water dimer
 - ◆ Time step errors cancel
 - ◆ Extrapolated D_e for AE and PP with SJ and BF wave functions within error bars of “exact” value

Acknowledgments...

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