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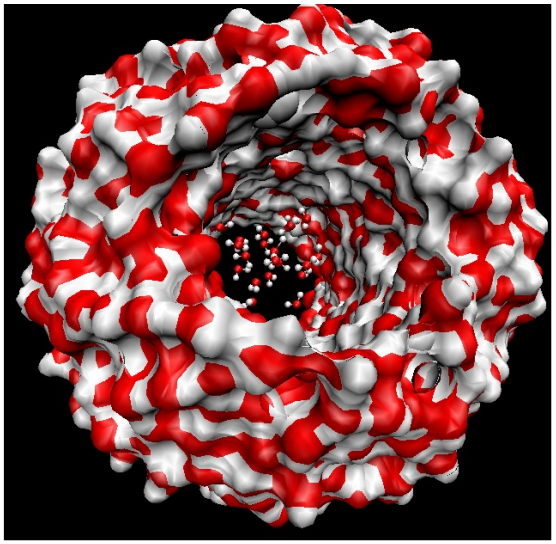

Water

a test for
SCCdftb/MM

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Summary

0.Why liquid water? fundamental test for condensed phase reactions

1.Bibliography: molecular models of water

2.SCCdftb/MM: corrections

3.Implementation of a dynamical QM/MM partition (switching waters)

4.Test on condensed phase systems: diffusion coefficient
- Proton
- Hydroxide
- Neutral water

Modelling condensed phase water

neutral water, acid, basic, autoionization, phase transition

Classical approximations (no explicit treatment of electrons)

MM, EVB (Warshel, Voth, Tuckerman)

Path Integrals

Full QM systems

Lagrangian: CPMD (Parrinello, Pratt), ADMP(Voth,Iyengar)

Linear Scaling: Siesta, Divide and Conquer. (AIMD,PM3,SCCdftb)

QM/MM

Ab initio/MM: Rode

SCCdftb/MM: → compromise between sampling and accuracy

SCCdftb/MM: corrections (Haibo and Yang)

$$E = \sum_{i}^{occ} \langle \psi_i | \hat{H}_0 | \psi_i \rangle \underbrace{- \frac{1}{2} \iint' \frac{n_0' n_0}{|\vec{r} - \vec{r}'|} + E_{XC}[n_0] - \int V_{XC}[n_0] n_0 + E_{ii}}_{E_{rep}[n_0]} + \underbrace{\frac{1}{2} \iint' \left(\frac{1}{|\vec{r} - \vec{r}'|} + \frac{\delta^2 E_{XC}}{\delta n \delta n'} \Big|_{n_0} \right) \delta n \delta n'}_{E_{2nd}}$$

gaussw

Repulsion $E_{rep}[n_0]$ $E_{rep}(O-H) = E_{rep}(O-H)_{orig} + a_1 \exp(-\frac{(r-a_2)^2}{a_3}) S(r)$

2nd order $E_{2nd} = \frac{1}{2} \sum_{A,B}^{N} \Delta q_A \Delta q_B \gamma_{AB}$

Hbond

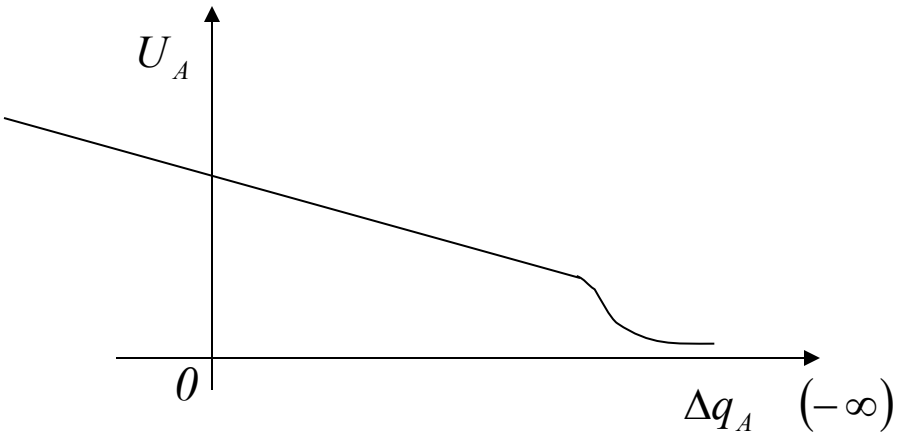
$$\gamma(X,H) = \exp(-\frac{(U_X + U_H)^{kl1}}{2} R^2) \gamma_0(X,H)$$

SCCdftb/MM: corrections (Haibo and Yang)

3rd order correction (Hubbard derivative)

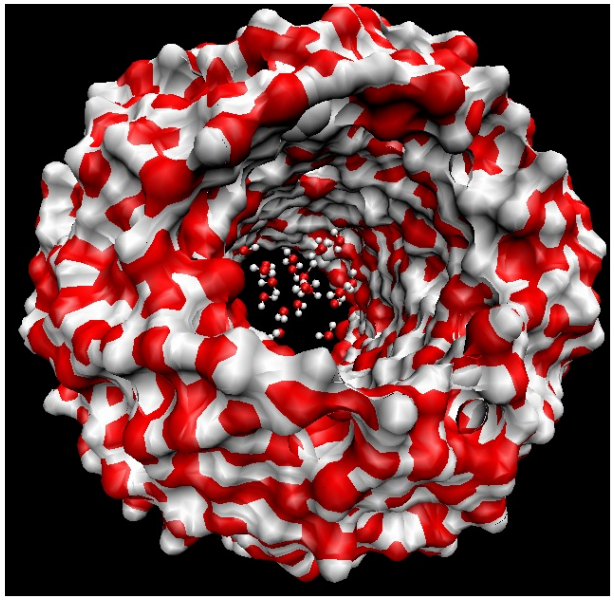
DHGA

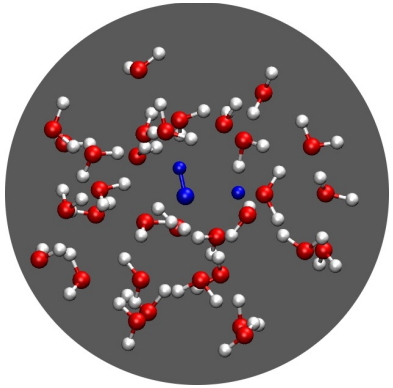
$$E_{3rd} = \frac{1}{6}\int\int'\int''\left(\left.\frac{\delta^3 E_{XC}}{\delta n\,\delta n'\,\delta n''}\right|_{n_0}\right)\delta n\,\delta n'\,\delta n'' = \frac{1}{6}\sum_A^N \frac{\partial U_A}{\partial q_A}\Delta q_A^3$$



$$f(\Delta q) = ae^{-b(\Delta q - q_0)^2}$$

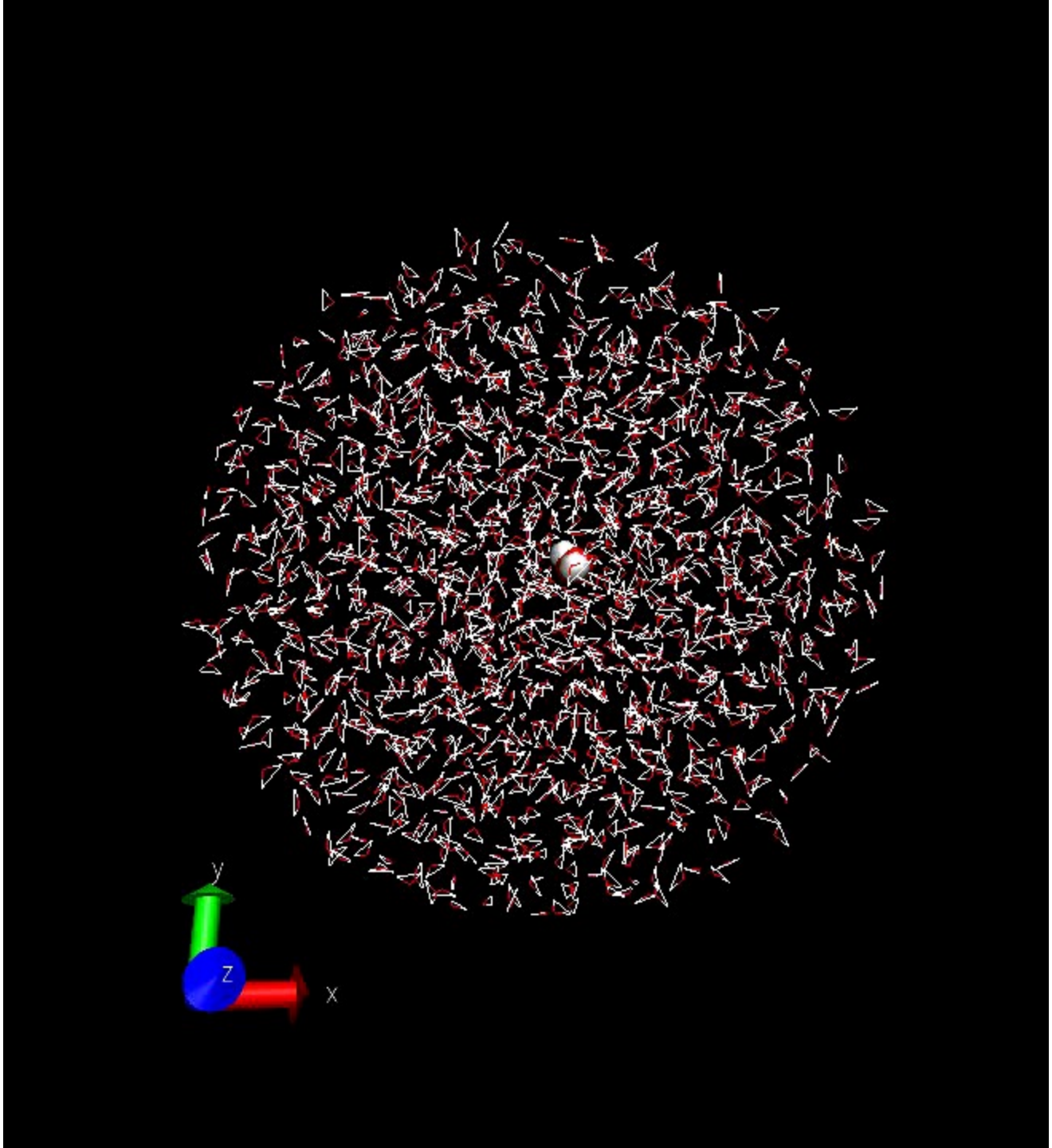
Switching waters in the QM/MM selection





Since solvent waters during a MD move in and move out of the QM/MM partition we will select dynamically the QM zone

- Exchange MM water moving in by a QM water moving out
- The composition of QM is always the same and it is selected by the distance to a central point

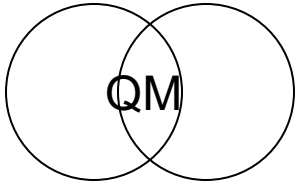

y
Z
X

Switching waters: criteria to select the QM waters

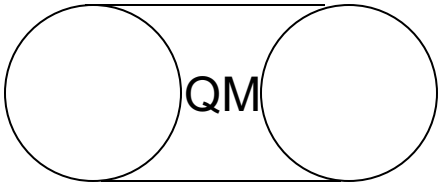
The waters that belong to the QM are reselected dynamically according to some criteria

- Around a point (fixed xyz or moving atom)

- Around two atoms



- Around the cylinder between two atoms



- Around the Center of excess charge (CEC)

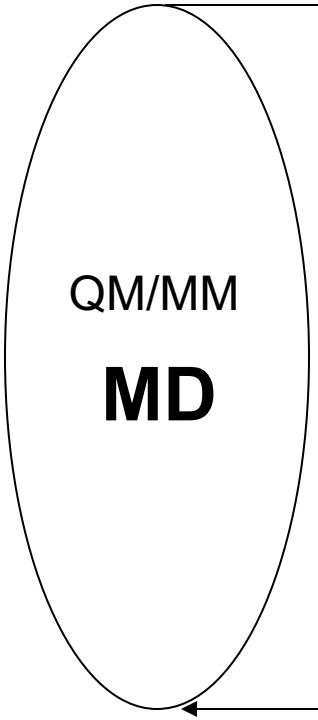
$$\xi_z = \sum_{i=1}^{N_H} r_z^{H_i} - \sum_{j=1}^{N_O} w^{O_j} r_z^{O_j} - \sum\sum f_{sw}(d_{O_j,H_i}) \cdot (r_z^{H_i} - r_z^{O_j})$$

- Around the closest proton or oxygen to the CEC

(see vmd)

Switching waters: implementation in charmm

rxncor: define pcec sele (qm .and. type O) end sele (qm .and. type H*) end*
sccdftb remove chrg 1 sele qm end TEMP 0.00 scft 0.00000001 –
swit sele (qm .and. type O) end sele ((.not. qm) .and. type O*) end*
swop 6 swfq 1 swpr 1.5



Build a list of distances of QM and MM waters with respect to the point.

Every *swfq* steps the lists are checked and updated

If r(O-MM) + swpr < r(O-QM)
the switch is performed on the XYZ arrays
(not for minimization!!)
Check connectivity
Update nonbonded lists

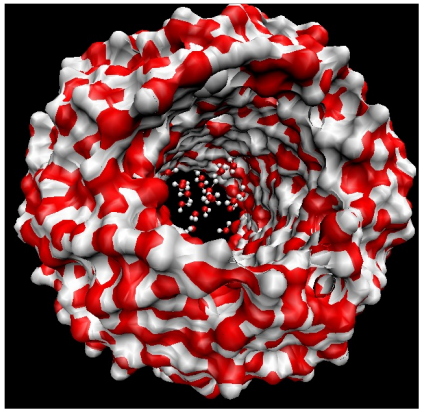
In our systems we ususally switch a water every 50 steps

Test: QM/MM systems

Solvated proton
Solvated OH^-
Neutral water (solvated water)

A 22 angstr. sphere of TIP3 waters with GSBP
300 K with Langevin+Stoch 20-22 angst., SHAKE for MM, 1fs timestep

QM: 6 angstr. around the target atom
90-150 atoms



SCCdftb corrections:
3rd order
hbond + gaussw
hbond + 3rd order + gaussw

Compute coefficient of diffusion and RDF

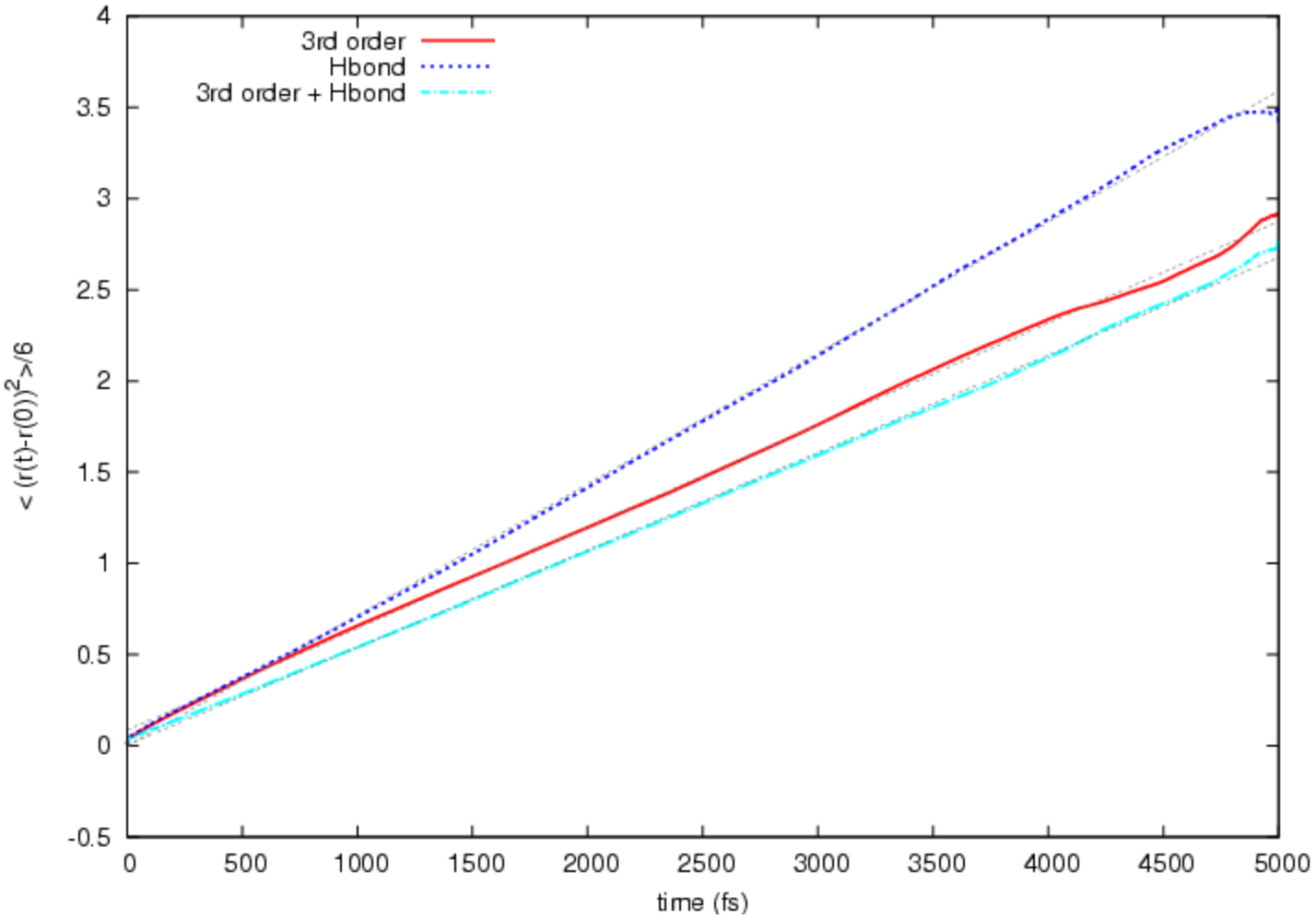
$$Diff = \lim_{t\to\infty} \frac{d}{dt} \frac{\left\langle (r(t) - r(0))^2 \right\rangle}{6}$$

H^+

$$Diff = \frac{d}{dt}\frac{\left\langle (r(t)-r(0))^2 \right\rangle}{6}$$

experimental
9.3E-4 Å²/fs

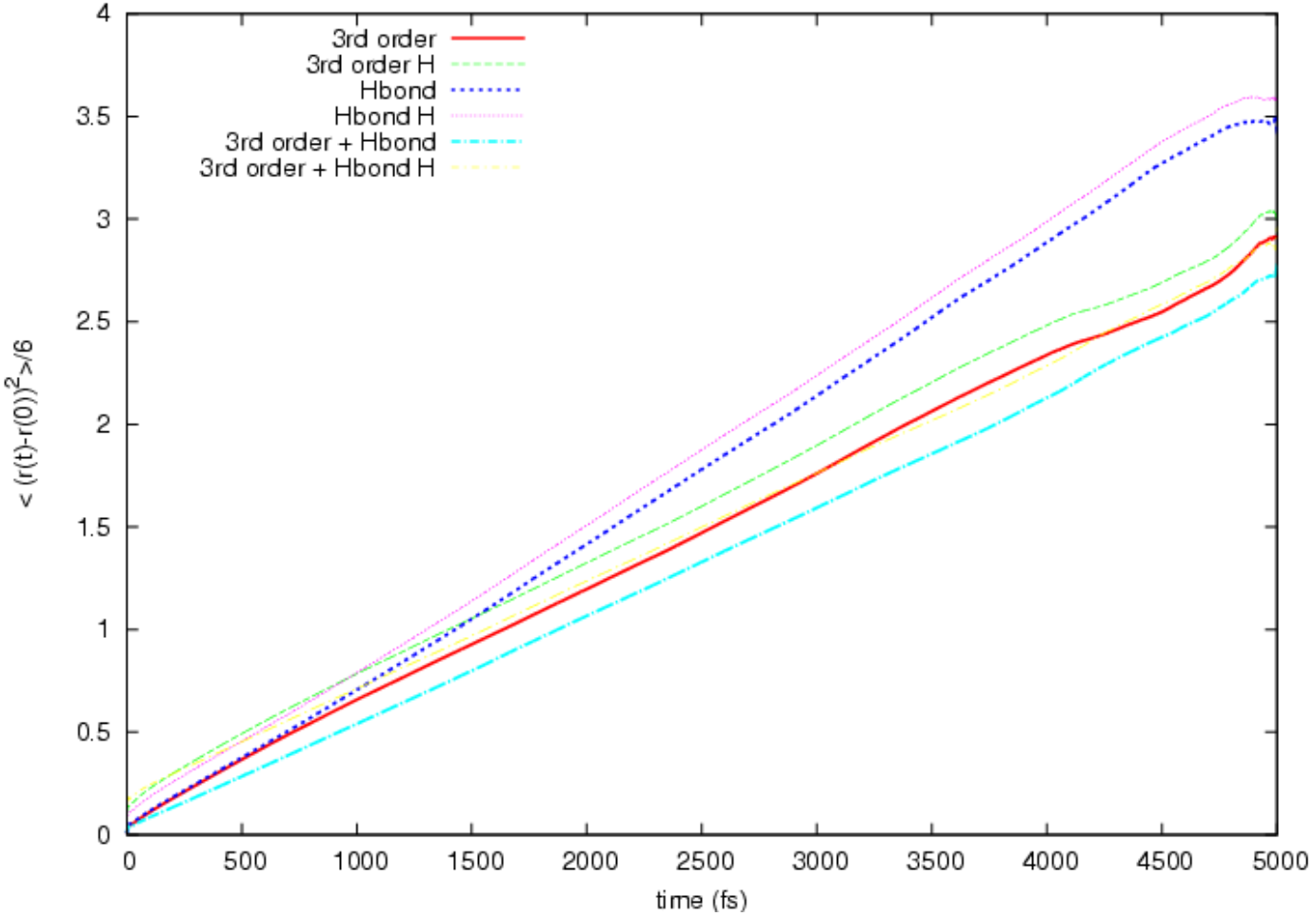
3rd order: 5.5E-4 Å²/fs
Hbond: 7.2E-4 Å²/fs
3rd+Hbond: 5.3E-4 Å²/fs



H^+ who's the proton? CEC vs closest H to CEC

experimental
9.3E-4 Å²/fs

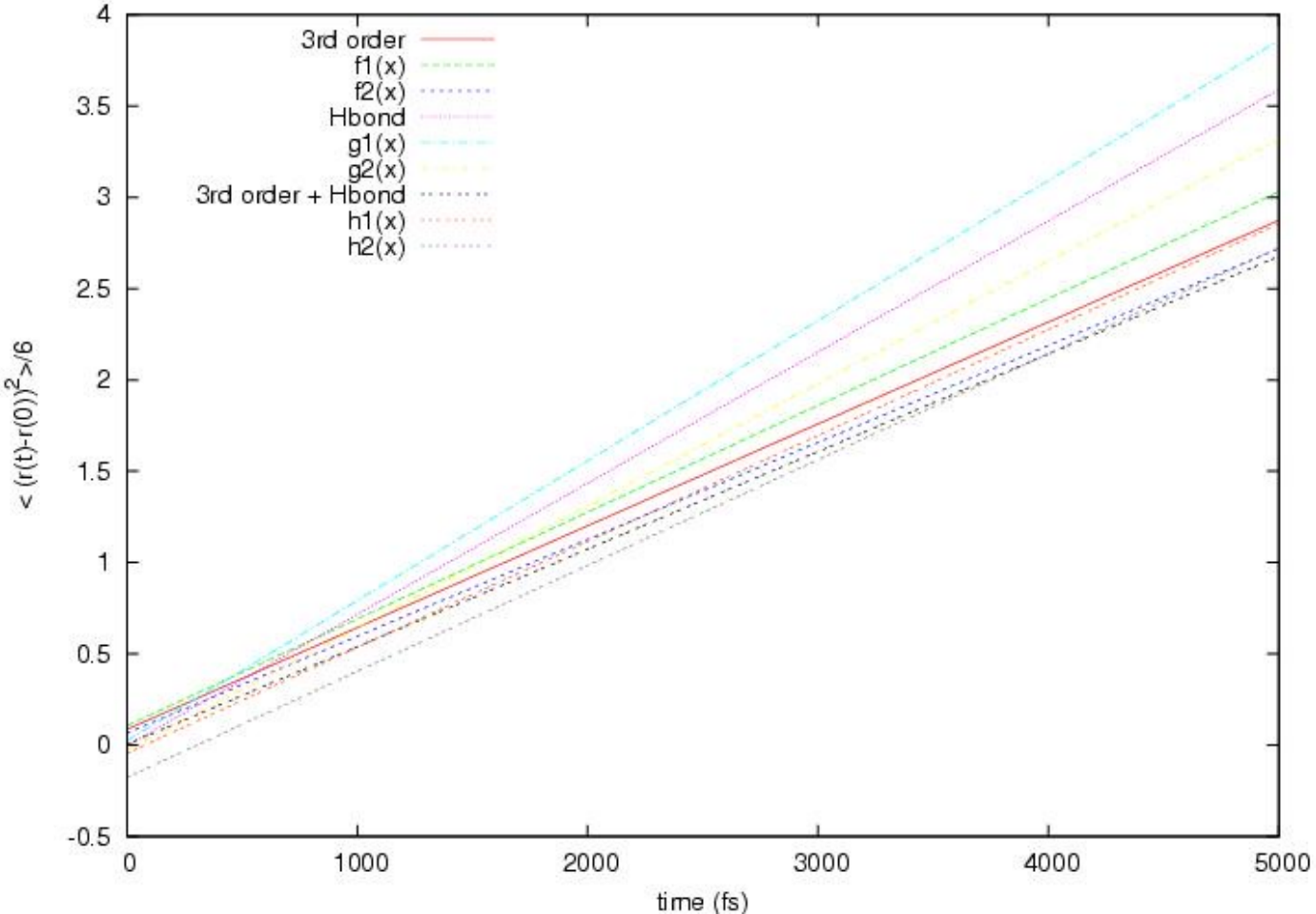
	CEC	H to CEC
3rd order:	5.5E-4 Å²/fs	5.6E-4
Hbond:	7.2E-4 Å²/fs	7.3E-4
3rd+Hbond:	5.3E-4 Å²/fs	5.3E-4



H^+ effect of the QM size

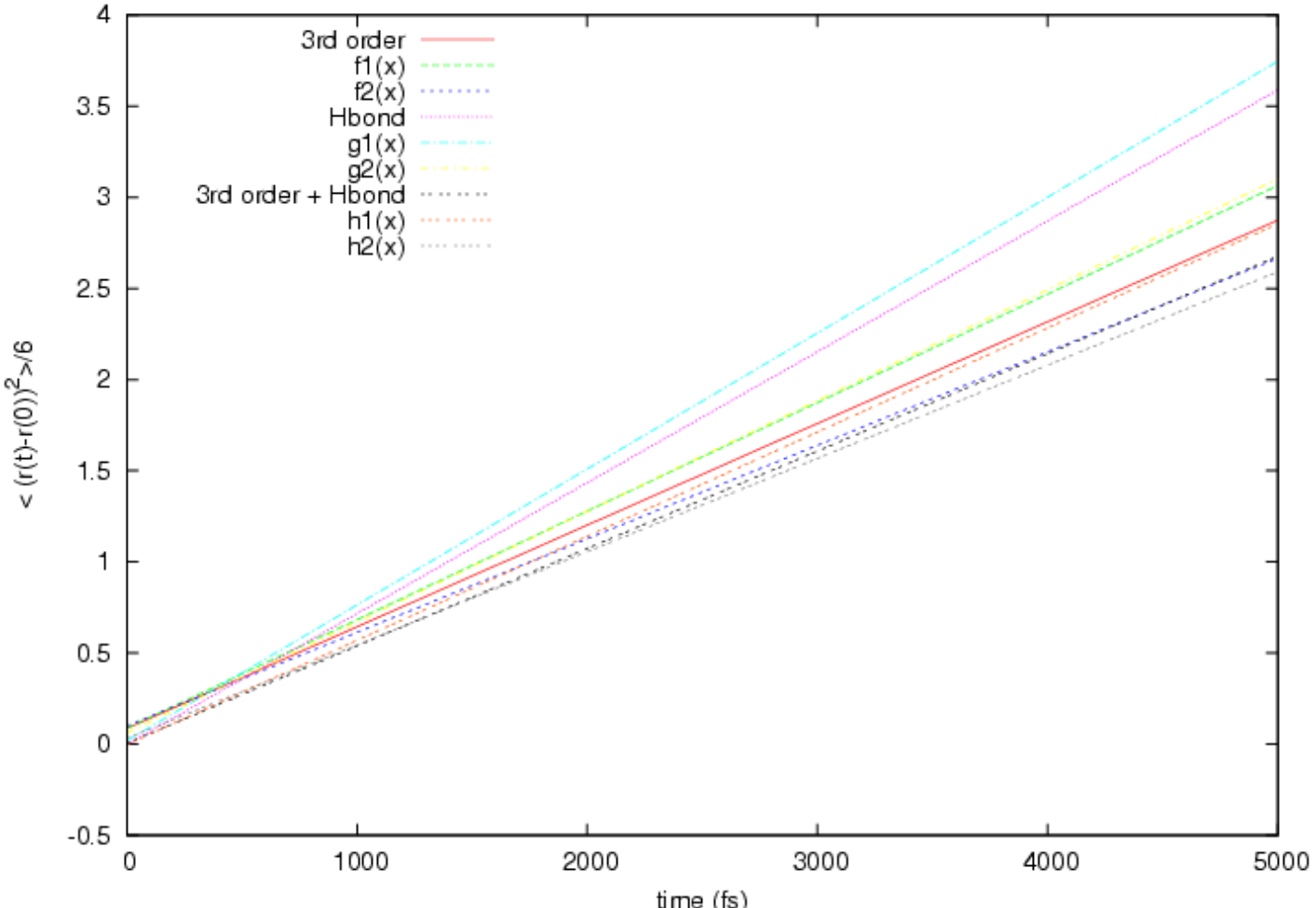
		bigQM	smallQM
3rd order:	5.5E-4 Å²/fs	5.8E-4	5.3E-4
Hbond:	7.2E-4 Å²/fs	7.6E-4	6.7E-4
3rd+Hbond:	5.3E-4 Å²/fs	5.8E-4	4.9E-4

experimental
9.3E-4 Å²/fs



H^+ effect of the edge of sphere

		1st 2.5ps	2nd 2.5ps
	3rd order: 5.5E-4 Å²/fs	6.0E-4	5.1E-4
experimental	Hbond: 7.2E-4 Å²/fs	7.4E-4	6.1E-4
9.3E-4 Å²/fs	3rd+Hbond: 5.3E-4 Å²/fs	5.7E-4	5.1E-4

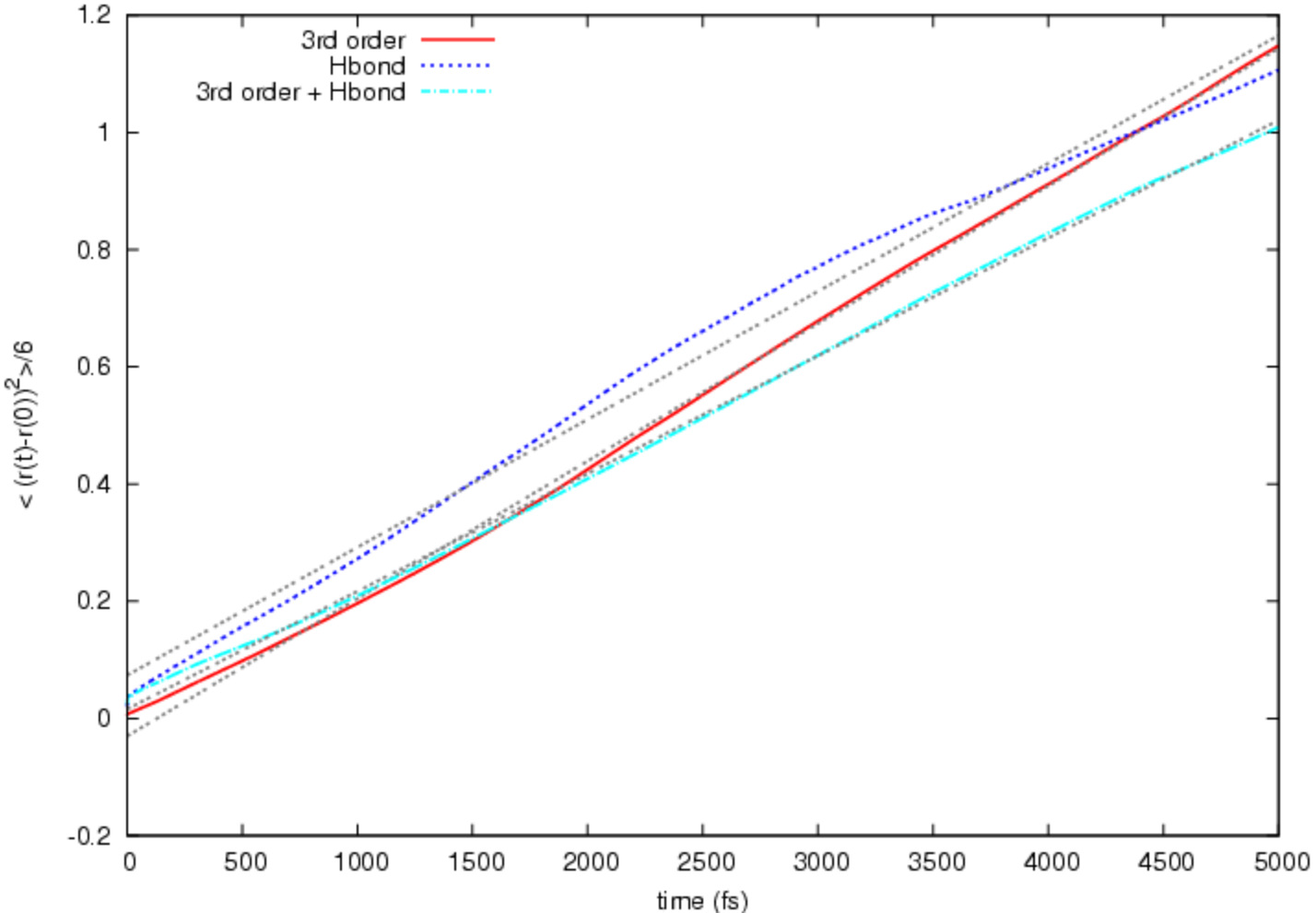


OH^- : Herr doktor Haibo Yu

$$Diff = \frac{d}{dt}\frac{\left\langle (r(t)-r(0))^2 \right\rangle}{6}$$

experimental
5E-4 Å²/fs

3rd order: 2.3E-4 Å²/fs
Hbond: 2.2E-4 Å²/fs
3rd+Hbond: 2.0E-4 Å²/fs

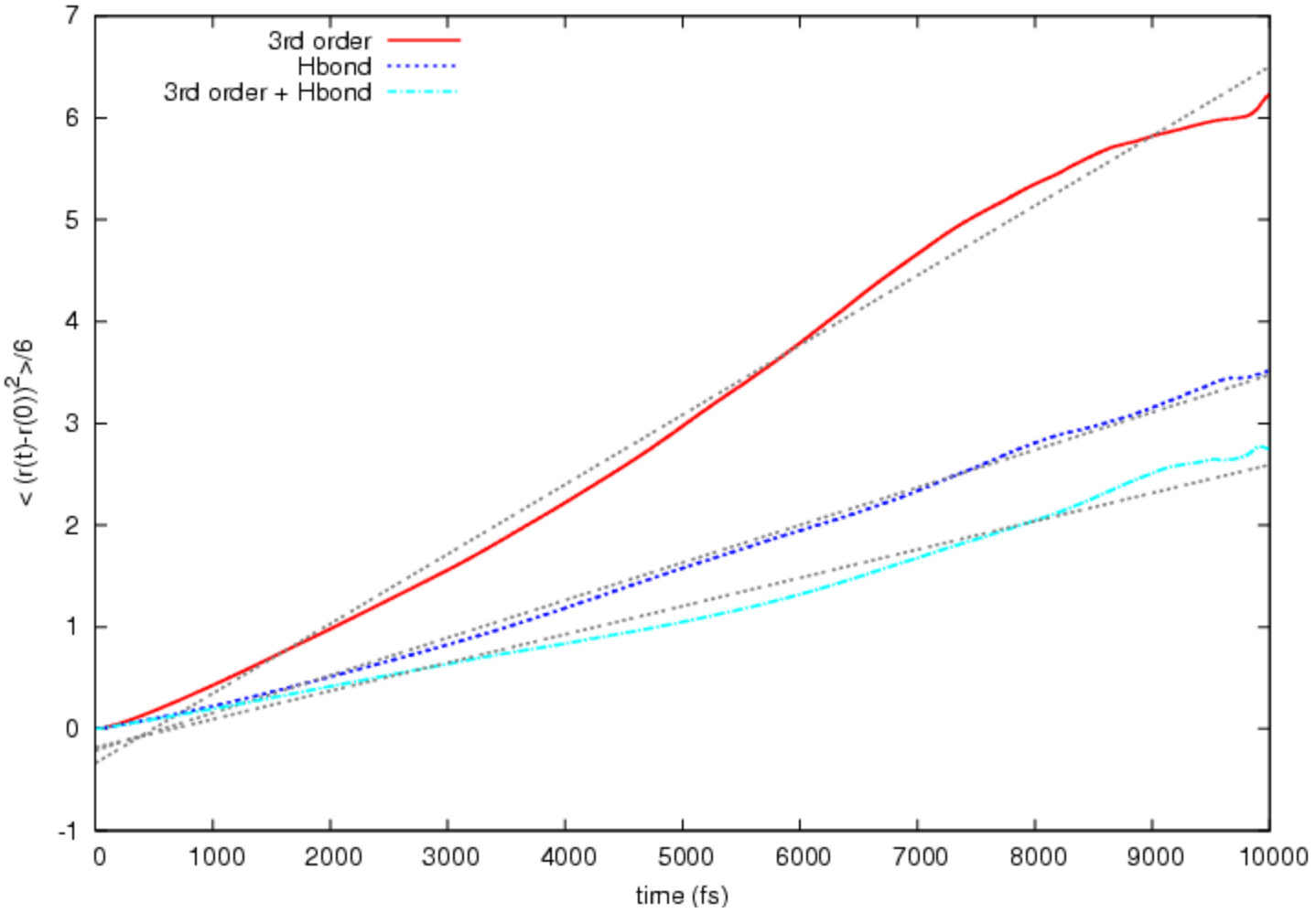


H_2O

$$Diff = \frac{d}{dt}\frac{\left\langle (r(t)-r(0))^2 \right\rangle}{6}$$

experimental
2.9E-4 Å²/fs

3rd order: 6.8E-4 Å²/fs
Hbond: 3.7E-4 Å²/fs
3rd+Hbond: 2.8E-4 Å²/fs



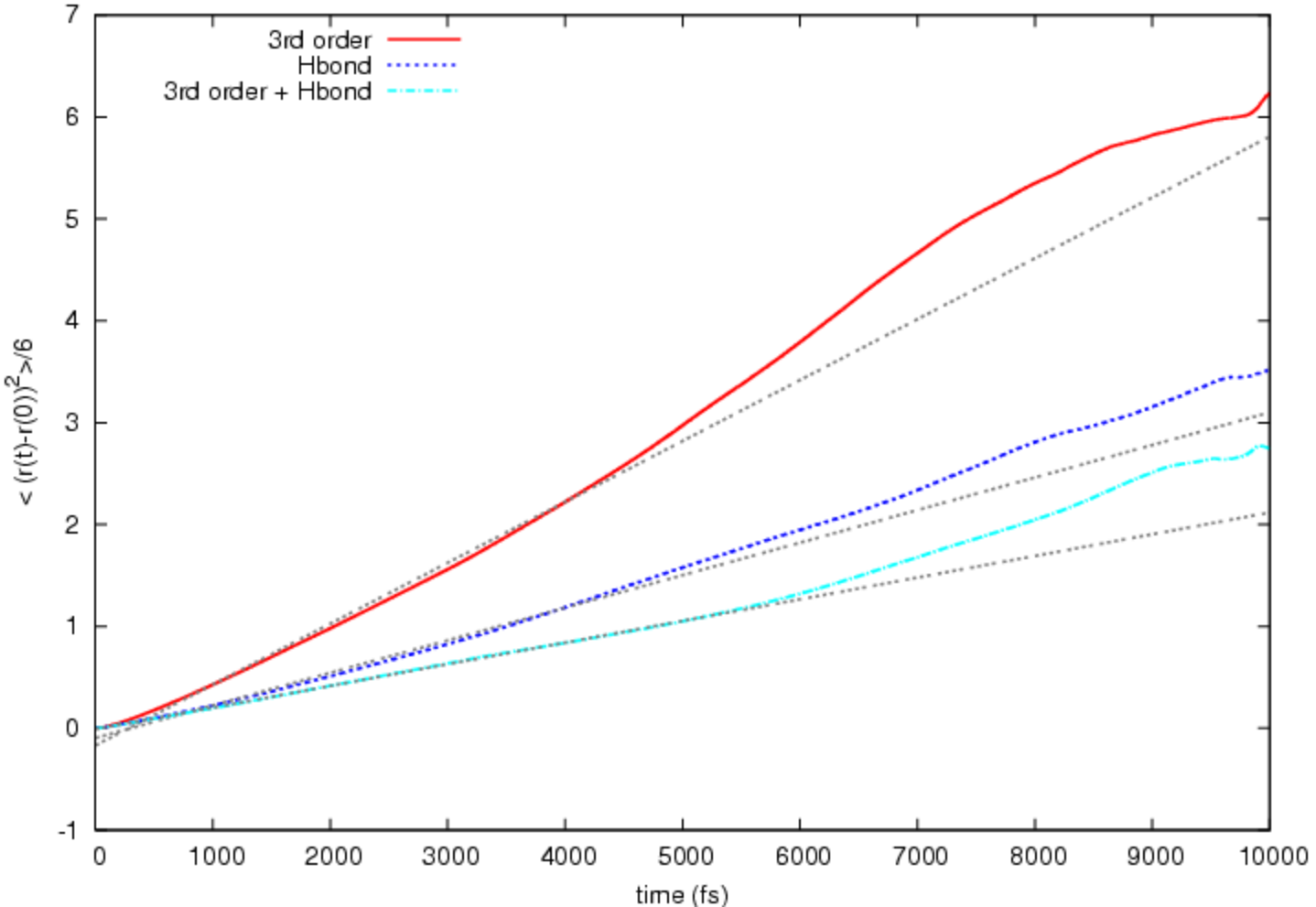
H_2O

1st 5ps

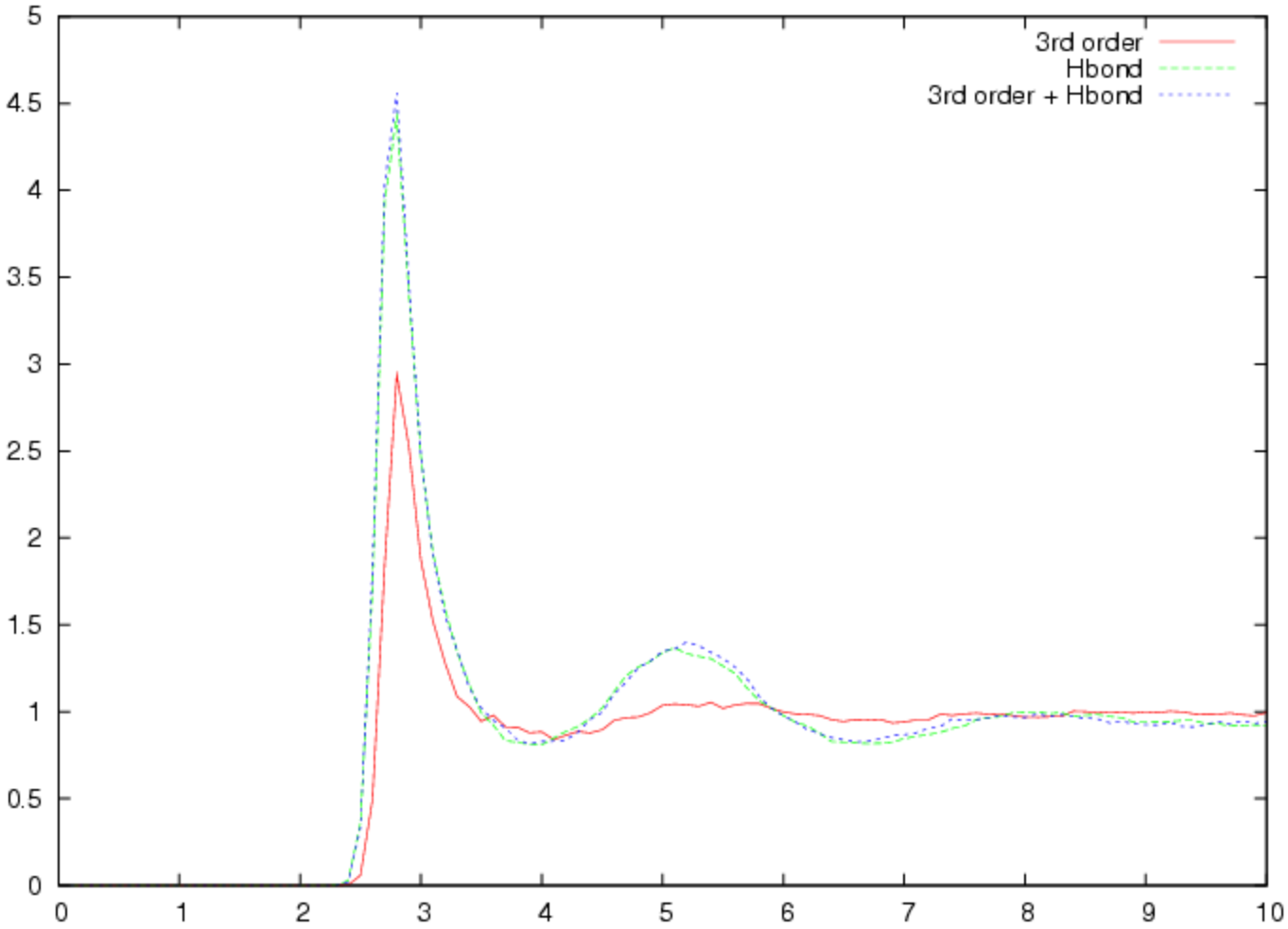
$$Diff = \frac{d}{dt}\frac{\left\langle (r(t)-r(0))^2 \right\rangle}{6}$$

experimental
2.9E-4 Å²/fs

3rd order: 6.0E-4 Å²/fs
Hbond: 3.2E-4 Å²/fs
3rd+Hbond: 2.1E-4 Å²/fs



H_2O: RDF gO-O


3rd order
Hbond
3rd order + Hbond
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
0
1
2
3
4
5
6
7
8
9
10


"That's all Folks!"