

Multiple Time Step Algorithms for Efficient Multiscale Molecular Dynamics Simulations in Ground and Excited States

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Abstract

Ab initio Molecular Dynamics (AIMD) is a versatile tool to determine static and dynamic properties of biomolecular and condensed phase systems in ground as well as electronically excited states. Unfortunately, the feasibility of AIMD simulations of extended systems is often limited by its high computational cost. Multiple Time Step (MTS) algorithms[1] exploit the timescale separation of nuclear forces to evaluate the slow forces only once every M MD steps, hence improving the computational efficiency of MD simulations.

We present here our implementation, and first applications, of two time-reversible MTS algorithms [2,3] in the Density Functional Theory (DFT) based *ab initio* Molecular Dynamics code, CPMD[4]. The timescale separation is achieved through introducing “reference” fast forces (F_{ref}) and slow “corrections” (ΔF). The first algorithm, based on *ab initio* evaluation of both F_{ref} and ΔF , uses quantum mechanical (QM) electronic structure methods of different accuracy; the second uses classical forces (based on force fields) in the reference steps and DFT in the correction steps, facilitating classical timescales with *ab initio* accuracy.

Multiple Time Step in Ab Initio Molecular Dynamics

- To reduce the computational cost of MD simulations, in MTS algorithms[1] the slow force components are evaluated at a lower frequency ($1/M$).

- The present MTS algorithm can be derived from the time-reversible Reference System Propagation Algorithm (r-RESPA) of Tuckerman and Martyna[1].

Algorithm Derivation (Liouville formalism):

Phase space propagator:

$$\Gamma(t) = e^{iL_t}\Gamma(0); \quad iL = \{\dots, H\} = \frac{p}{m}\partial_x + F\partial_p = iL_x + iL_p \quad (1)$$

Introduction of “slow” and “fast” force components in AIMD

$$F = F_{\text{ref}} + \Delta F; \quad \Delta F = F - F_{\text{ref}}; \quad iL = iL_x + iL_p + iL_{p\Delta} \quad (2)$$

Trotter factorisation, introduction of two time-step lengths, dt and $Dt=Mdt$:

$$e^{iL_Dt} = e^{iL_{p\Delta}Dt/2} \prod_{i=1}^M \left[e^{iL_p \frac{dt}{2}} e^{iL_x dt} e^{iL_p \frac{dt}{2}} \right] e^{iL_{p\Delta}Dt/2} \quad (3)$$

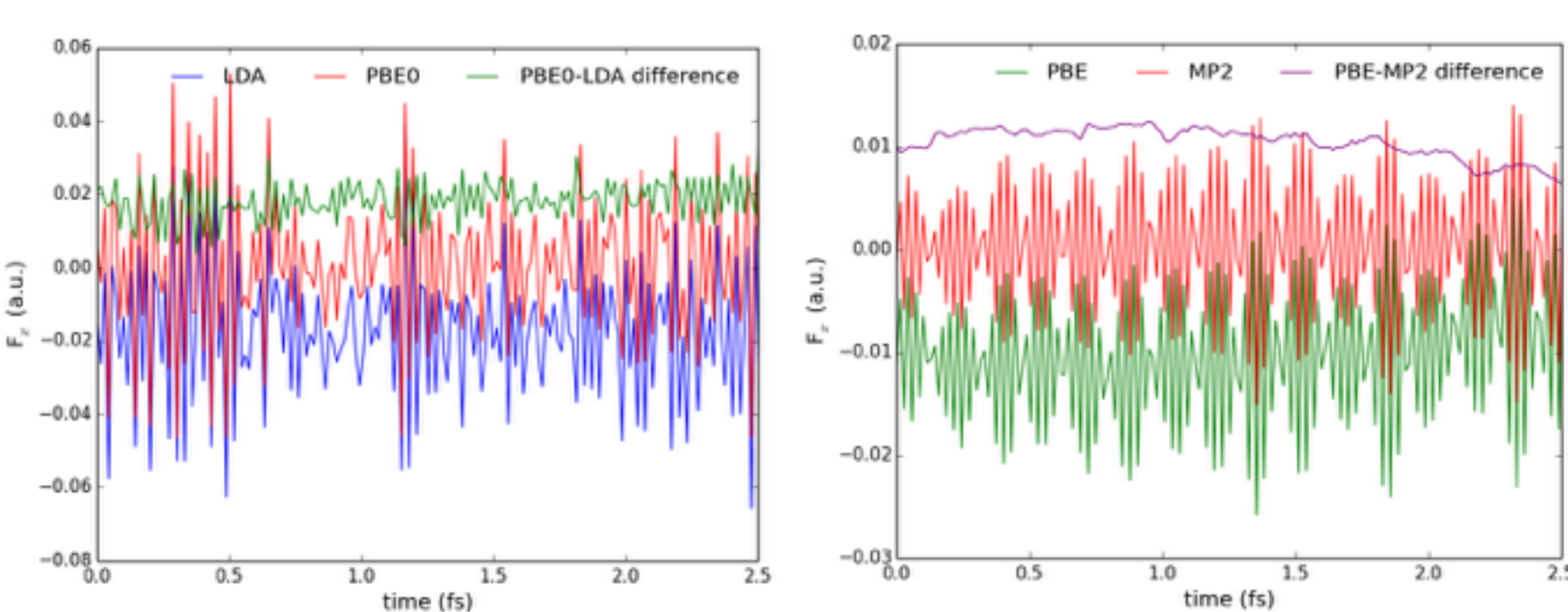


Fig.1 Time behaviour of the x component, nuclear forces and force correction ΔF in eq. (2). a) LDA, PBE0 and PBE0-LDA difference on an Oxygen atom in liquid water b) PBE, MP2 and MP2-PBE difference on the H-bond acceptor in water dimer. ΔF varies on a longer timescale compared to the absolute force.

Time gain:

- Ideal speedup: $S=M/(1+Mf) \sim M$, where $f=T_{\text{CPU}}^{\text{reference}}/T_{\text{CPU}}^{\text{higher accuracy}}$.
- If T_{high} = period of the fastest vibration of the system, $Dt^{\text{MAX}} = T/\pi$, $M^{\text{MAX}} \sim 10$.

MTS Dynamics in the CPMD Code

We implemented the following features in the CPMD code[4]:

- MTS for Born-Oppenheimer MD (BOMD), with QM reference and correction:
 - NVE or NVT, in combination with available thermostats (e.g. Langevin[5]).
 - DFT based: Full QM and QM/MM MD.
 - Interfaces with TURBOMOLE v6.2 and GAUSSIAN G09[6], to use electronic methods beyond DFT in the correction steps (available for full QM only).
- MTS for QM/MM with classical reference and QM-based correction:
 - NVE or NVT, in combination with available thermostats (e.g. Langevin[5]).

Test Systems: Computational Details

System	Acetone (1)	Acetone (2)	Water Dimer	Liquid Water
# Molecules	1 (+ 3000 wat.)	1 (+ 3000 wat.)	2	32
QM box (Å)	33x33x33	33x33x33	15x15x15	9.939x9.939x9.939
Basis sets High/Low	PW(70Ry)/PW(70Ry)	PW(70Ry)/PW(70Ry)	PW(90Ry)/aug-cc-pVTZ	PW(70Ry)/PW(70Ry)
Electronic Methods	PBE/PBE0	FF / PBE	PBE/MP2	LDA/PBE0
Inner/Outer Time Step (fs)	0.48/4.8	1.00/2.00	0.36/1.80	0.24/0.96

Accuracy and Efficiency Evaluation

Quality of the trajectories evaluated on the base of:

- Fluctuations of the total energy: $\varepsilon = \frac{1}{N} \sum_{i=1}^N \left| \frac{E_i - \bar{E}}{\bar{E}} \right|$
- Statical (structure) and dynamical (vibrational spectra) properties

Fig.2: Logarithm of the total energy fluctuation along a trajectory 26ps-long (upper panel) and vibrational spectra (lower panel) for an acetone molecule in aqueous solution, obtained with Velocity Verlet BOMD (PBE and PBE0 functionals) and with PBE/PBE0-MTS dynamics.

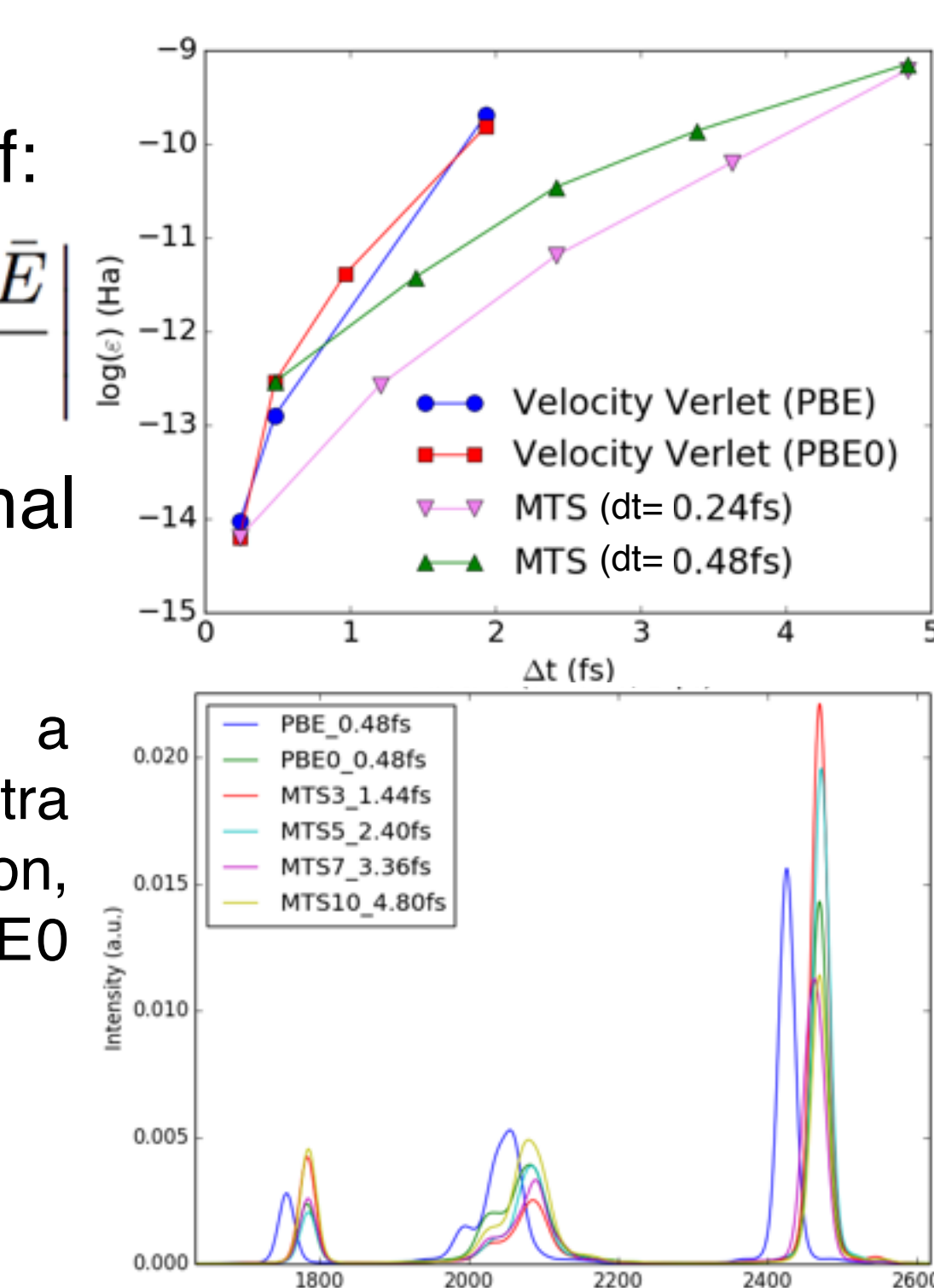
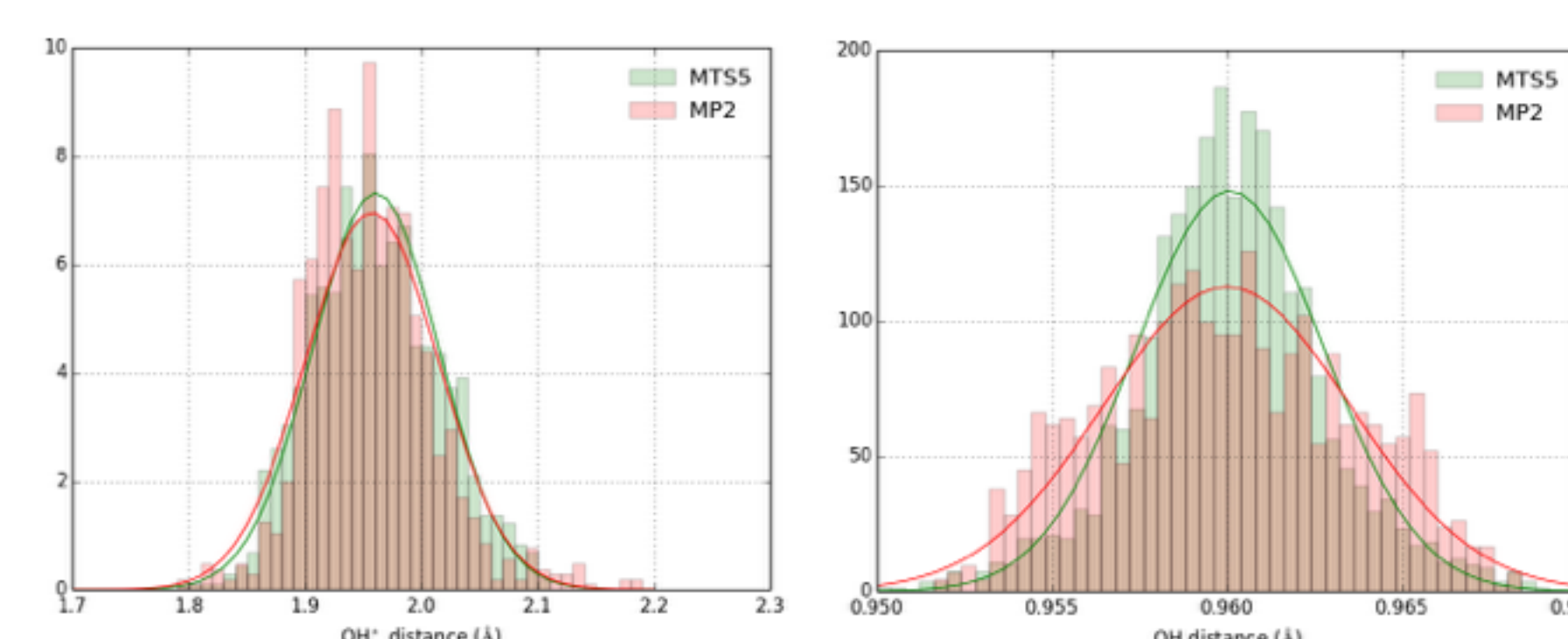
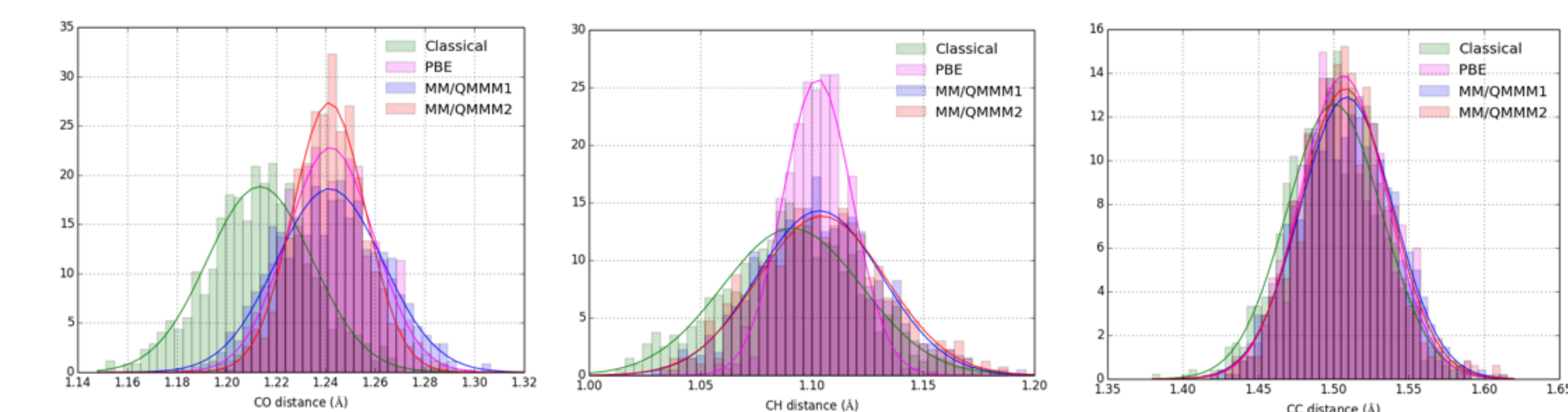


Fig.3: Hydrogen bond (OH*) and OH bond distance distributions in water dimer, along an MP2 trajectory (red) and a PBE/MP2-MTS5 trajectory (green).

Fig.4: Oxygen-oxygen (a) and intramolecular oxygen-hydrogen (b) radial distribution functions, obtained with LDA-VV MD (blue), PBE0-VV (red) and LDA/PBE0-MTS4 MD (magenta). For comparison, the same quantities from Ref.[7a] and [7b] are also shown in orange and green. (c) Summary of the performances of the MTS scheme: CPU time per step, speedup (S) and efficiency (W) as a function of the outer time step value Dt .

Dt (fs)	T_{CPU} (s)	S	W
0.36	92.2	1.0	100%
0.72	58.8	1.6	82%
1.08	44.4	2.1	72%
1.44	36.9	2.6	66%
1.80	32.1	3.0	61%
2.52	27.0	3.5	52%

Fig.5: C-O, C-H and C-C bond distributions in an acetone molecule solvated in water, along a classical trajectory using an AMBER force field (green), a PBE-VV trajectory (magenta), and two MM/QMMM MTS trajectories corresponding to $M=1$ (blue) and $M=2$ (red).



Further Developments and Ongoing Work

To improve the computational performances, the present MTS scheme will be combined with:

- A Generalised Langevin stochastic thermostat[5] to further increase the outer time step.
- An algorithm for the on-the-fly adaptation of the outer time step, to always maintain the optimal balance between accuracy and efficiency.
- Machine Learning techniques and schemes for fast evaluation of exact exchange (see box below), for better efficiency.

Moreover the MTS scheme will be extended to excited state dynamics.

Fast Evaluation of Exact Exchange (EEX) Energies and Potentials

- Ongoing development of a new scheme within plane-wave/pseudo-potential, Kohn-Sham DFT, based on spectral splitting of the potential:
 - Short-range (expanded on atomic basis, precomputed and stored).
 - Long-range (residual function on a coarser grid, then interpolated).

$$\bar{\rho}_{ij}(\mathbf{R}_\psi) = \psi_i(\mathbf{R}_\psi)\psi_j(\mathbf{R}_\psi) - \sum_{\alpha} \sum_l c_{\alpha}^l \chi_{\alpha}^l(\mathbf{R}_\psi) \quad c_{\alpha}^l = \langle \chi_{\alpha}^l | \psi_i \psi_j \rangle \quad (4)$$

$$\text{Standard CPMD expression:} \quad v_{ij}(\mathbf{R}) = \text{FFT}^{-1} \left\{ \frac{4\pi}{G^2} [\text{FFT} \psi_i(\mathbf{R}) \psi_j(\mathbf{R})] \right\} \quad (5)$$

$$\text{Present expression:} \quad v_{ij}(\mathbf{R}_\psi) = \sum_{\alpha} \sum_l c_{\alpha}^l v_{\chi_{\alpha}^l}(\mathbf{R}_\psi) + \hat{P}_{\mathbf{R}_\psi}(\mathbf{R}_\psi) [\bar{v}_{ij}(\mathbf{R}_\psi)] \quad (6)$$

(time gain ~ a factor 16)

References

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