Ab initio molecular dynamics techniques

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CPMD–CP2K tutorial – 08/04/2010

Outline

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Lagrangian mechanics

- Lagrangian $\mathcal{L}$ for a system consisting of n generalized degrees of freedom $\mathbf{q} = \{q_i\}_{i \in N}$:

$$\mathcal{L}(\mathbf{q}, \dot{\mathbf{q}}) = \mathcal{K}(\mathbf{q}, \dot{\mathbf{q}}) - \mathcal{V}(\mathbf{q})$$

  where $\mathcal{K}$ is the kinetic energy and $\mathcal{V}$ the potential energy

- Equations of motion generated by Euler-Lagrange equation

$$\frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{q}_i} - \frac{\partial \mathcal{L}}{\partial q_i} = 0$$

- Conserved quantity:

$$\mathcal{H}(\mathbf{q}, \dot{\mathbf{q}}) = \mathcal{K}(\mathbf{q}, \dot{\mathbf{q}}) + \mathcal{V}(\mathbf{q})$$

Equations of motion: classical MD

N atoms, $n = 3N$ Cartesian degrees of freedom $\{\mathbf{R}_I\}_{I \in N}$

$$\mathcal{L}(\{\mathbf{R}_I\}, \{\dot{\mathbf{R}}_I\}) = \mathcal{K}(\{\dot{\mathbf{R}}_I\}) - \mathcal{V}(\{\mathbf{R}_I\}) = \sum_I \frac{m_I}{2} \dot{\mathbf{R}}_I^2 - \mathcal{V}(\{\mathbf{R}_I\})$$

Defining momentum $\mathbf{p}_I$ and force $\mathbf{f}_I$ according to

$$\mathbf{p}_I = \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{R}}_I} = m_I \dot{\mathbf{R}}_I, \qquad \mathbf{f}_I = \frac{\partial \mathcal{L}}{\partial \mathbf{R}_I} = -\frac{\partial \mathcal{V}}{\partial \mathbf{R}_I}$$

we recover Newton's equations from the Euler-Lagrange equation as

$$\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{R}}_I} = \frac{\partial \mathcal{L}}{\partial \mathbf{R}_I} \quad \Rightarrow \quad \dot{\mathbf{p}}_I = -\frac{\partial \mathcal{V}}{\partial \mathbf{R}_I} \quad \Rightarrow \quad m_I \ddot{\mathbf{R}}_I = \mathbf{f}_I$$

Lagrangian mechanics: Car-Parrinello MD

$$\mathcal{L}_{\mathrm{CP}} = \sum_I \frac{m_I}{2}\dot{\mathbf{R}}_I^2 + \sum_i \mu\langle\dot{\phi}_i \mid \dot{\phi}_i\rangle - \langle\psi_0 \mid \mathcal{H}_e \mid \psi_0\rangle + \sum_{i,j}\Lambda_{ij}(\langle\phi_i \mid \phi_j\rangle - \delta_{ij})$$

where the four terms respectively represent:

- Classical kinetic energy
- Electronic kinetic energy (fictitious)
- Potential energy
- and some Constraints for imposing orbital orthonormality $\langle\phi_i \mid \phi_j\rangle = \delta_{ij}$ with the use of Lagrange multipliers Λ_{ij}

Equations of motion: Car-Parrinello MD

Propagation of the atomic positions and of the orbitals

$$
\begin{aligned}
m_I \ddot{\mathbf{R}}_I &= -\frac{\partial}{\partial \mathbf{R}_I} \langle \psi_0 \mid \mathcal{H}_e \mid \psi_0 \rangle \\
\mu \ddot{\phi}_i &= -\frac{\partial}{\partial \phi_i^*} \langle \psi_0 \mid \mathcal{H}_e \mid \psi_0 \rangle + \sum_j \Lambda_{ij} \phi_j
\end{aligned}
$$

CP Lagrangian – DFT / plane waves framework

$$\begin{aligned}\mathcal{L}_{\rm CP} &= \sum_I \frac{m_I}{2}\dot{\mathbf{R}}_I^2 + \mu\sum_i\sum_{\mathbf{G}} \mid \dot{c}_i(\mathbf{G}) \mid^2 - E^{KS}[\{\mathbf{G}\},\{\mathbf{R}_I\}] \\ &\quad + \sum_{i,j}\Lambda_{ij}\Big(\sum_{\mathbf{G}} c_i^*(\mathbf{G})c_j(\mathbf{G}) - \delta_{ij}\Big)\end{aligned}$$

and the associated Euler-Lagrange equations:

$$\begin{aligned} m_I\ddot{\mathbf{R}}_I &= -\frac{\partial E^{KS}}{\partial \mathbf{R}_I} \\ \mu\ddot{c}_i(\mathbf{G}) &= -\frac{\partial E^{KS}}{\partial c_i^*(\mathbf{G})} + \sum_j \Lambda_{ij}c_j(\mathbf{G}) \end{aligned}$$

Lagrangian mechanics: Born-Oppenheimer MD

$$\mathcal{L}_{\mathrm{BO}} = \sum_I \frac{m_I}{2}\dot{\mathbf{R}}_I^2 - \langle\psi_0 \mid \mathcal{H}_e \mid \psi_0\rangle + \sum_{i,j}\Lambda_{ij}(\langle\phi_i \mid \phi_j\rangle - \delta_{ij})$$

and the associated Euler-Lagrange equations:

$$\begin{aligned} m_I\ddot{\mathbf{R}}_I &= -\frac{\partial}{\partial \mathbf{R}_I}\min_{\{\phi_i\}}\{\langle\psi_0 \mid \mathcal{H}_e \mid \psi_0\rangle\} \\ 0 &= -\frac{\partial}{\partial \phi_i^*}\langle\psi_0 \mid \mathcal{H}_e \mid \psi_0\rangle + \sum_j \Lambda_{ij}\phi_j \end{aligned}$$

Outline

Integration: velocity Verlet algorithm

$$\dot{\tilde{\mathbf{R}}}_I(t+\delta t) = \dot{\mathbf{R}}_I(t) + \frac{\delta t}{2M_I}\mathbf{F}_I(t) \tag{1}$$

$$\mathbf{R}_I(t+\delta t) = \mathbf{R}_I(t) + \delta t\dot{\tilde{\mathbf{R}}}_I(t+\delta t) \tag{2}$$

$$\text{calculate} \qquad \mathbf{F}_I(t+\delta t) \tag{6}$$

$$\dot{\mathbf{R}}_I(t+\delta t) = \dot{\tilde{\mathbf{R}}}_I(t+\delta t) + \frac{\delta t}{2M_I}\mathbf{F}_I(t+\delta t) \tag{8}$$

(10)

Integration: velocity Verlet algorithm

$$\dot{\tilde{\mathbf{R}}}_I(t+\delta t) = \dot{\mathbf{R}}_I(t) + \frac{\delta t}{2M_I}\mathbf{F}_I(t) \quad (1)$$

$$\mathbf{R}_I(t+\delta t) = \mathbf{R}_I(t) + \delta t\dot{\tilde{\mathbf{R}}}_I(t+\delta t) \quad (2)$$

$$\dot{\tilde{c}}_i(t+\delta t) = \dot{c}_i(t) + \frac{\delta t}{2\mu}f_i(t) \quad (3)$$

$$c'_i(t+\delta t) = c_i(t) + \delta t\dot{\tilde{c}}_i(t+\delta t) \quad (4)$$

$$c_i(t+\delta t) = c'_i(t+\delta t) + \sum_j X_{ij}c_j(t) \quad (5)$$

$$\text{calculate} \quad \mathbf{F}_I(t+\delta t) \quad (6)$$

$$\text{calculate} \quad f_i(t+\delta t) \quad (7)$$

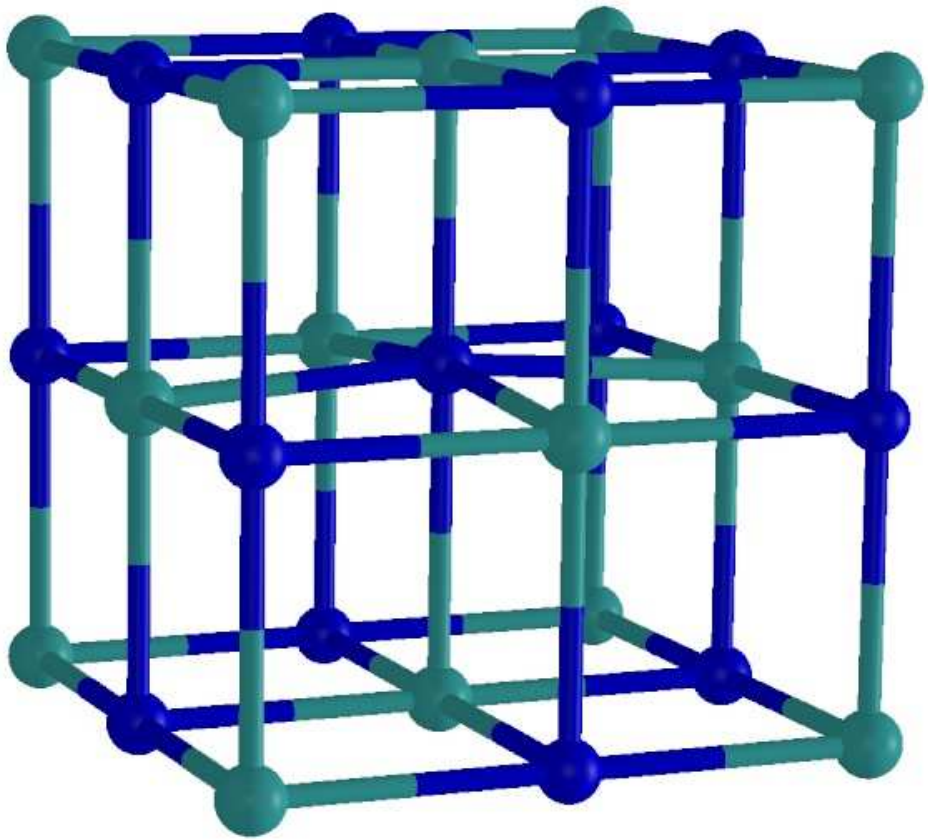
$$\dot{\mathbf{R}}_I(t+\delta t) = \dot{\tilde{\mathbf{R}}}_I(t+\delta t) + \frac{\delta t}{2M_I}\mathbf{F}_I(t+\delta t) \quad (8)$$

$$\dot{c}'_i(t+\delta t) = \dot{\tilde{c}}_i(t+\delta t) + \frac{\delta t}{2\mu}f_i(t+\delta t) \quad (9)$$

$$\dot{c}_i(t+\delta t) = \dot{c}'_i(t+\delta t) + \sum_j Y_{ij}c_j(t+\delta t) \quad (10)$$

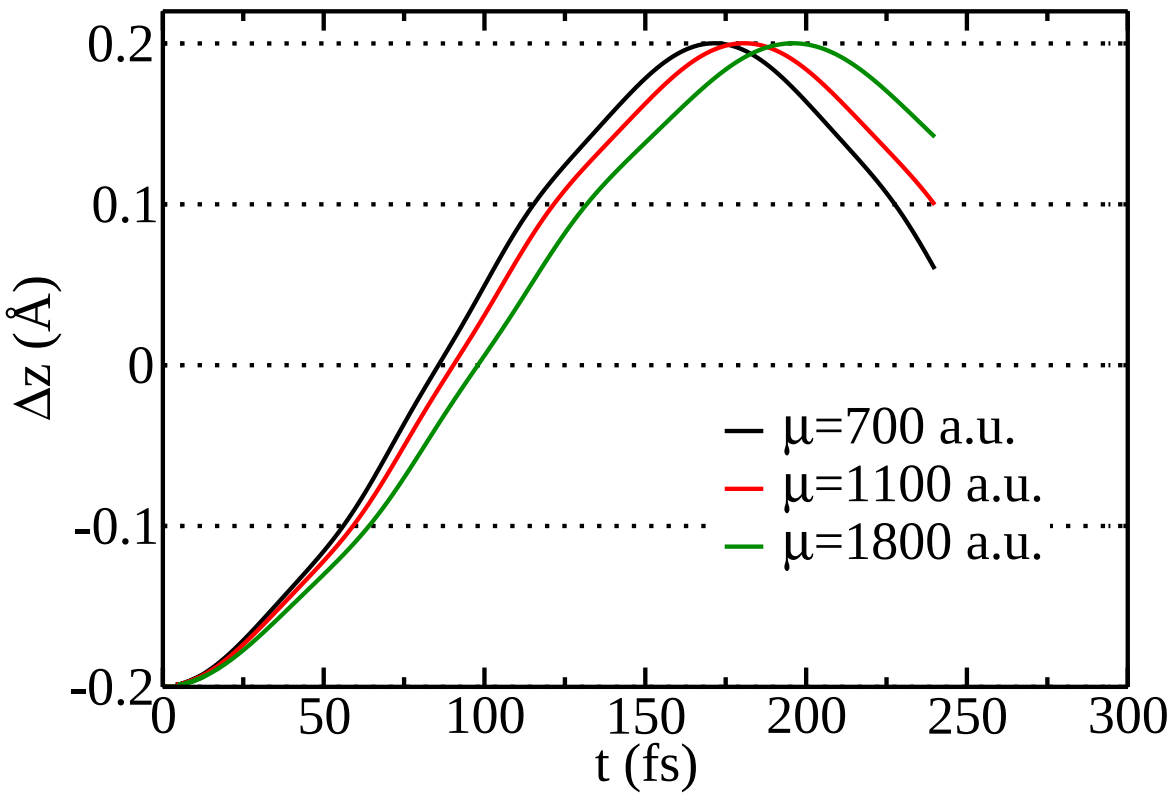
Outline

Dynamics of Na+ in a NaCl matrix



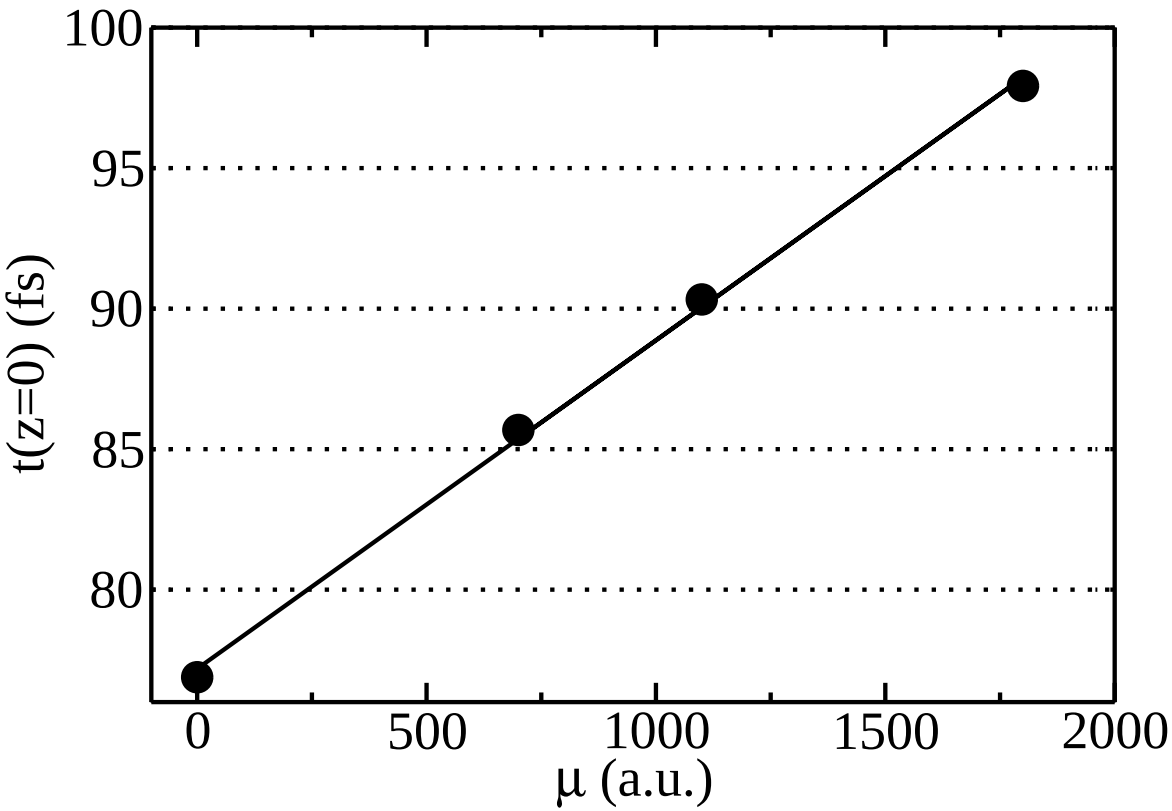
Central Na^+ displaced at 0.2 Å from its equilibrium position

Dynamics of Na+ in a NaCl matrix

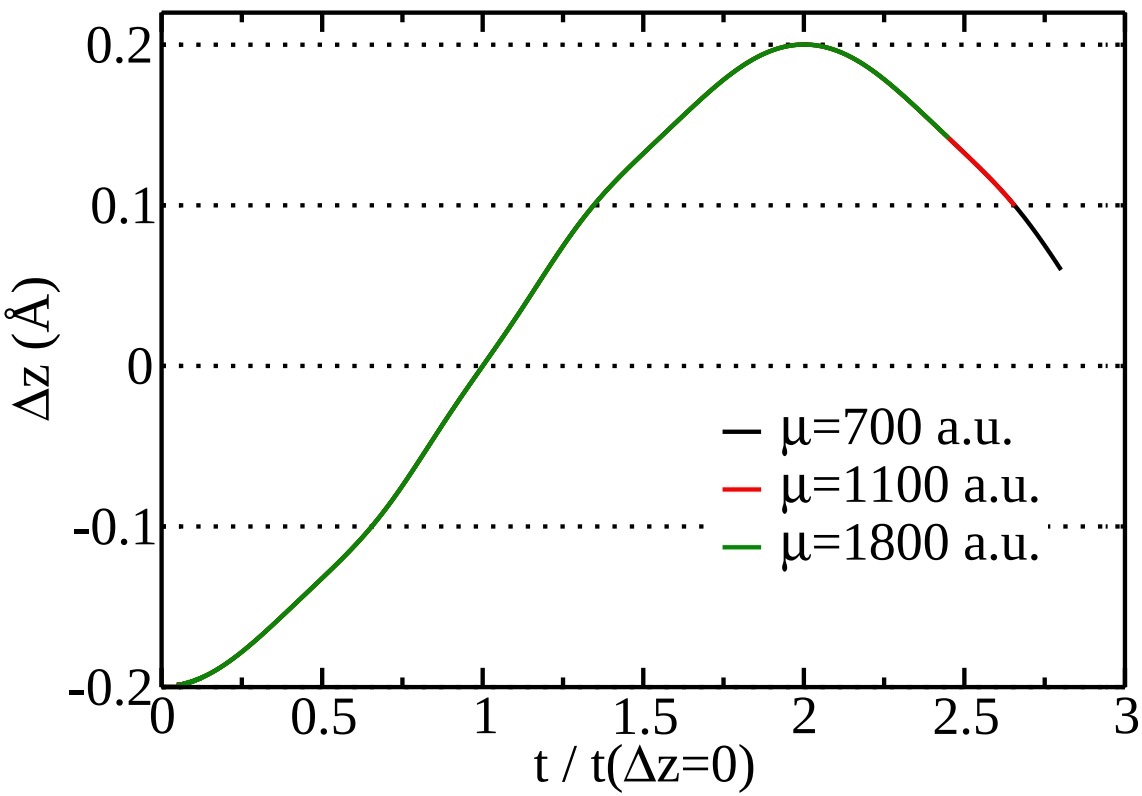


Evolution of $\Delta z = z - z_{eq}$ with time for different values of μ.

First passage time at $\Delta z = 0$



Dynamics with renormalization of time



Interpretation: renormalization of the mass

$$\omega_{\mathrm{BO}} = \omega_{\mathrm{CP}} \sqrt{\frac{M_I'}{M_I}}$$

where $M_I' = M_I + \Delta_\mu M_I$, and in a "rigid ion" approximation

$$\Delta_\mu M_I = \frac{2}{3} \frac{m_e}{\hbar^2} \sum_j \mu \langle \phi_j^I \mid -\frac{\hbar^2}{2m_e} \nabla_j^2 \mid \phi_j^I \rangle$$

Some conditions on μ

- μ is a "non-physical" parameter controlling the time scale of the "classical" Car Parrinello electronic dynamics
- It has to be assigned an optimal value such that
  - adiabatic separation between artificial electronic and real ionic motion is ensured
  - time step Δt is as large as possible

Some conditions on μ

- μ is a "non-physical" parameter controlling the time scale of the "classical" Car Parrinello electronic dynamics
- It has to be assigned an optimal value such that
  - adiabatic separation between artificial electronic and real ionic motion is ensured
  - time step Δt is as large as possible
- Upper limit for μ: frequency of the slowest electronic motion determined by HOMO-LUMO energy gap must be higher than fastest nuclear motion:

$$\omega_e^{\min} \approx \left(\frac{E_{gap}}{\mu} \right)^{1/2} > \omega_n^{\max}$$

- Example: system with hydrogen atoms: $\mu \approx 500$ a.u., $\Delta t \approx$5–10 a.u. $=$ 0.1–0.2 fs

Outline

CPMD simulation of 32 water molecules

δt=5 a.u. (0.12 fs)

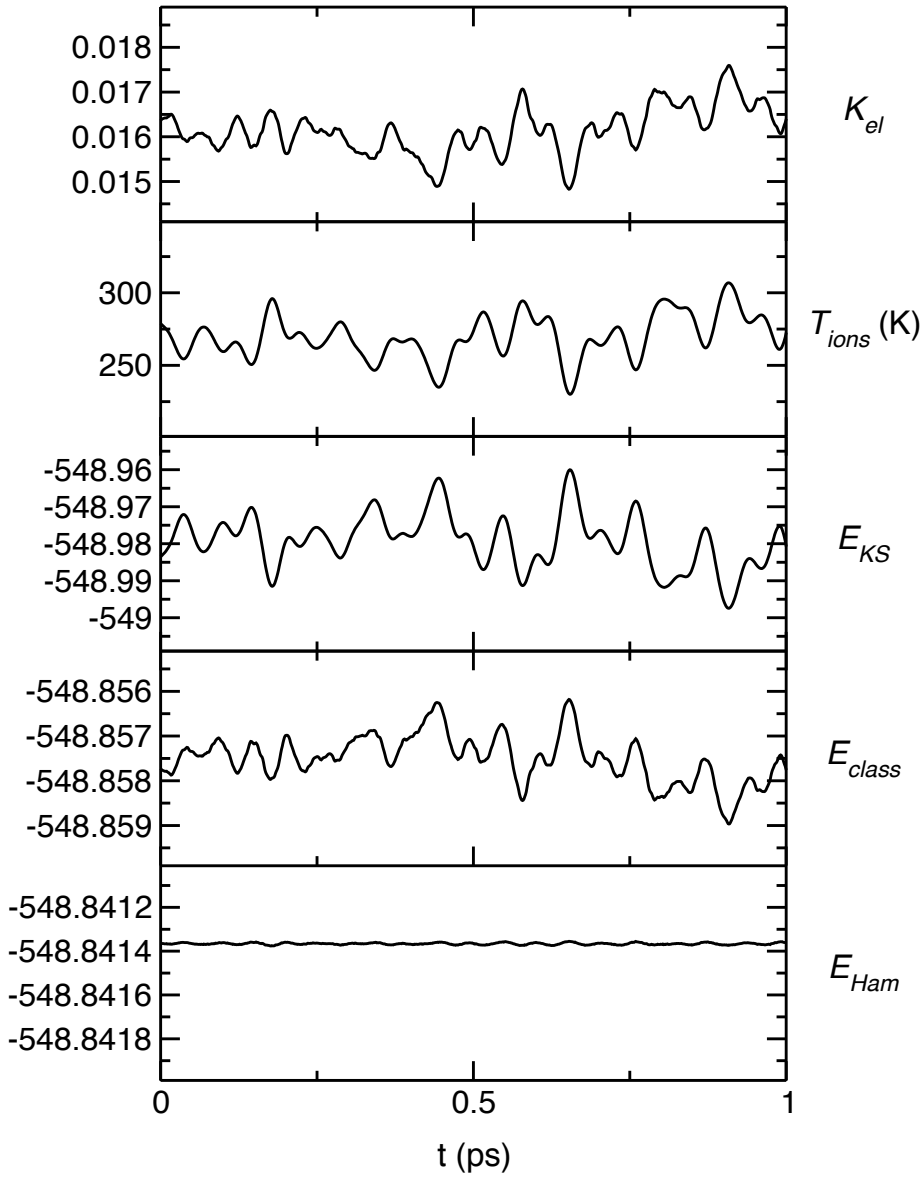
L=9.865 Å

TM pseudos

E_{cut}=70 Ry

BLYP functional

μ=500 a.u.



Stability of BO and CP compared (PW)

CPMD results for 8 Si atom model system (10 Ry, $\mu = 300$ a.u.)
CP and BO molecular dynamics for 1 ps of trajectory

Method	Time step (au)	Convergence (au)	Conservation (au/ps)	Time (s)
CP	5	–	6×10^{-8}	3230
CP	7	–	1×10^{-7}	2310
CP	10	–	3×10^{-7}	1610
BO	10	10^{-6}	1×10^{-6}	16590
BO	50	10^{-6}	1×10^{-6}	4130
BO	100	10^{-6}	6×10^{-6}	2250
BO	100	10^{-5}	1×10^{-5}	1660
BO	100	10^{-4}	1×10^{-3}	1060

Characteristic parameters for different simulations of 32 water molecules (PW)

T=350 K; ρ=0.905 g.cm^{-3}; TM pseudos; E_{cut}=70 Ry

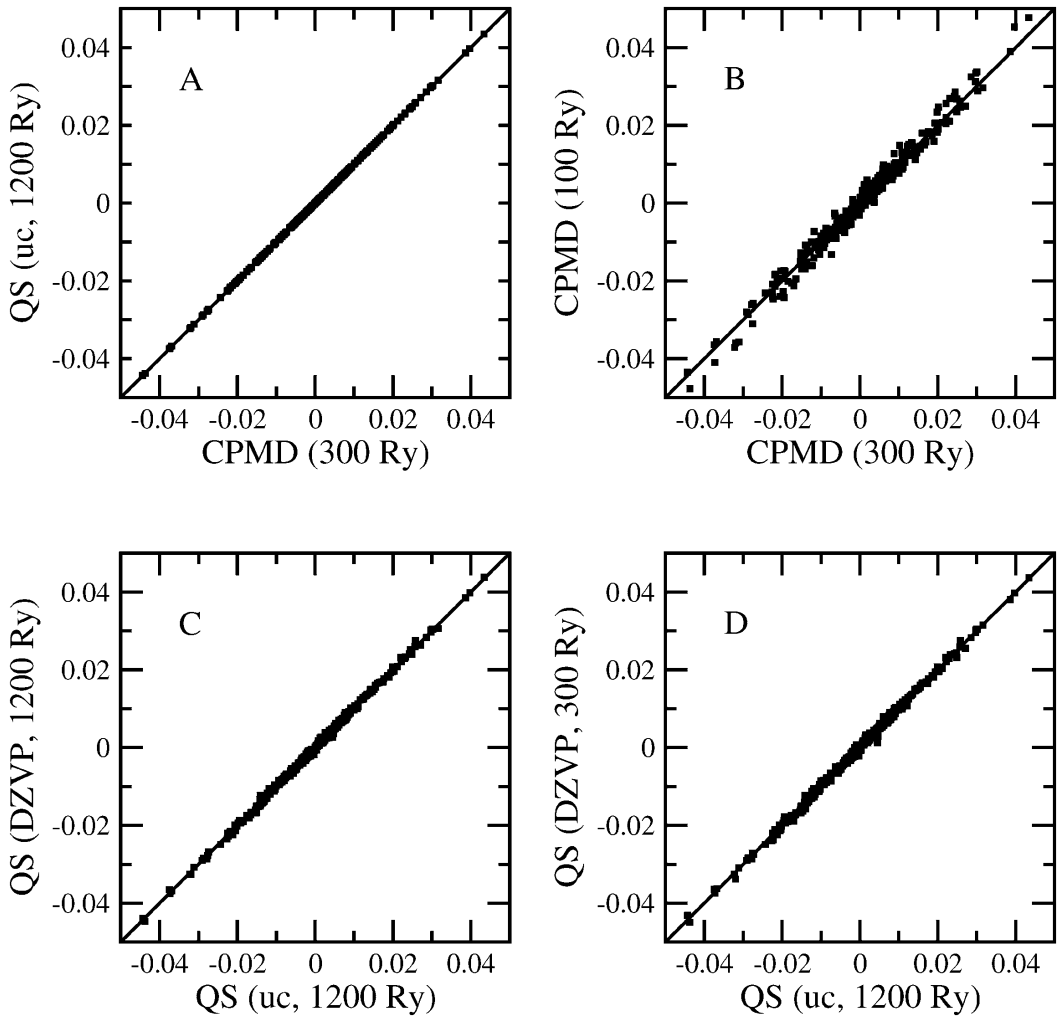
Simulation	Time step (au)	Convergence (au)	μ (au)	Relative Time (s)
CP	3	–	300	1.74
CP	4	–	500	1.29
CP	5	–	700	1.00
BO	20	10^{-4}	–	2.08
BO	20	10^{-5}	–	2.07
BO	20	10^{-6}	–	2.98
BO	20	10^{-7}	–	3.87

Energy drifts ans standard deviations for different simulations of 32 water molecules (PW)

T=350 K; ρ=0.905 g.cm^{-3}; TM pseudos; E_{cut}=70 Ry

Simulation	Physical energy		Conserved energy	
	drift (K.ps^{-1})	std (K)	drift (K.ps^{-1})	std (K)
CP300	0.276	1.02	0.007	0.004
CP500	0.736	1.61	0.012	0.006
CP700	3.070	2.37	0.019	0.008
BO4	2.980	0.16	2.980	0.159
BO5	1.584	0.13	1.584	0.129
BO6	0.092	0.12	0.092	0.119
BO7	0.033	0.11	0.033	0.113

BO in CPMD vs. QUICKSTEP: forces for 32 water molecules



uc: 253 basis functions per water molecule; DZVP: 23 basis functions per water molecule; GTH pseudopotentials

BO in CPMD vs. QUICKSTEP: energies for 64 water molecules

CPMD	70 Ry	85 Ry	100 Ry	150 Ry	200 Ry
MAD	15.5	10.8	3.6	1.9	0.0
RMSD	7.7	4.2	1.8	0.7	0.0

QUICKSTEP (TZV2P)	200 Ry	240 Ry	280 Ry	340 Ry	380 Ry
MAD	16.7	6.5	5.8	5.3	4.9
RMSD	5.9	2.3	2.2	2.0	1.8

QUICKSTEP (340 Ry)	DZVP	TZVP	TZV2P	QZV2P	QZV3P
MAD	11.1	9.3	5.3	5.2	4.6
RMSD	5.1	4.0	2.0	2.1	1.9

Ref: CPMD – 200 Ry

RMSD: Root mean square deviation

MAD: Maximum absolute deviation (in 10^{-3}a.u.)

Outline

Comparison of BO and CP dynamics

BO MD	**CP MD**
Exactly on BO surface, more accurate in principle	Always slightly off BO surface, less accurate
$\delta t \approx$ ionic time scales	$\delta t <$ ionic time scales
Diagonalization or minimization expensive at every time step	Only orthogonalization, far less expensive time steps
Not stable against deviation from BO surface	Stable
	Need to choose μ

References

- Dominik Marx and Jürg Hutter,
  Ab Initio Molecular Dynamics: Basic Theory and Advanced Methods
  Cambridge University Press, Cambridge 2009
- J. VandeVondele, M. Krack, F. Mohamed, M. Parrinello, T. Chassaing and J. Hutter, *Comp. Phys. Commun.* **167**, 103–128, 2005