

Extended Lagrangian BOMD in FHI-aims

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and Claudia Draxl ^{a)}

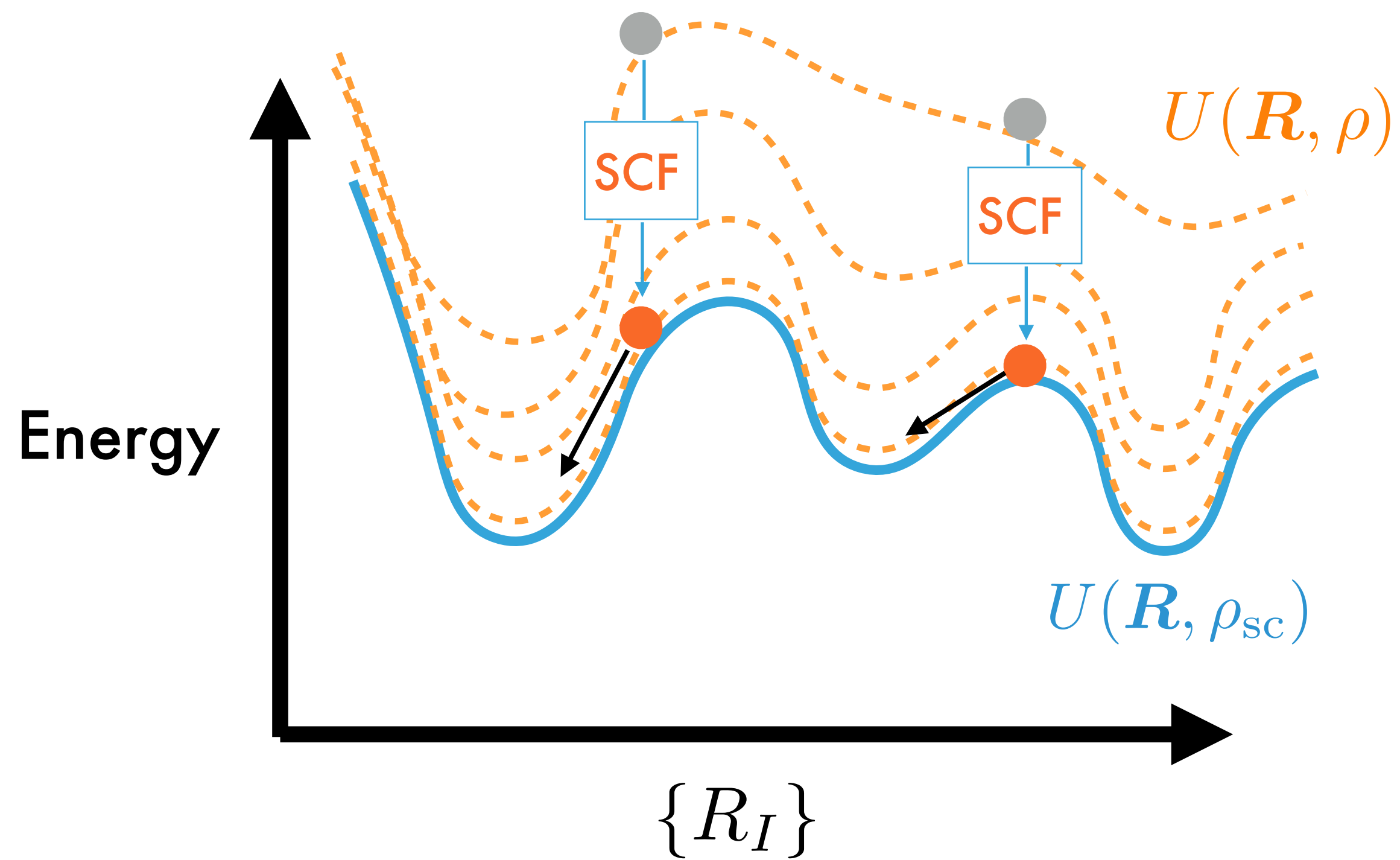
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Potential Energy Surface (PES)



Forces, energies calculated on the fly

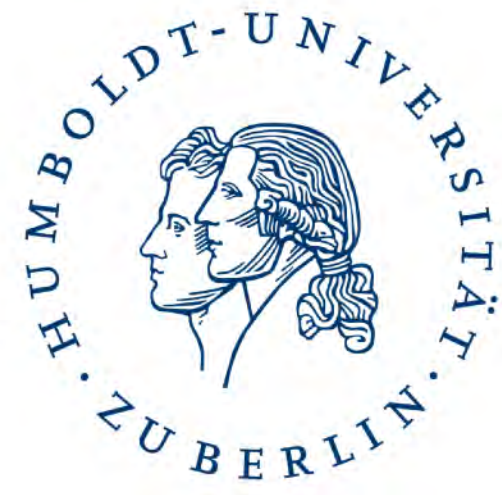
$$H[\rho]\Psi_i = \epsilon_i\Psi_i$$

SCF

$$\rho = \sum_{i \in \text{occ}} f_i |\Psi_i|^2$$

Cost + Error! ρ_{sc}

Density functional theory



Ab Initio Born-Oppenheimer Molecular Dynamics (BOMD)



Can we avoid the need of self consistency?



Main Concepts of Extended Lagrangian BOMD (XL-BOMD)



1. Introduction of Shadow PES for approximate density n
2. Include approximate density n as a dynamical field variable
3. Derive equations of motion in adiabatic limit

A. M. N. Niklasson, Phys. Rev. Lett. **100**, 123004 (2008)

A. M. N. Niklasson, J. Chem. Theory Comput. **16(6)**, 3628 (2020)

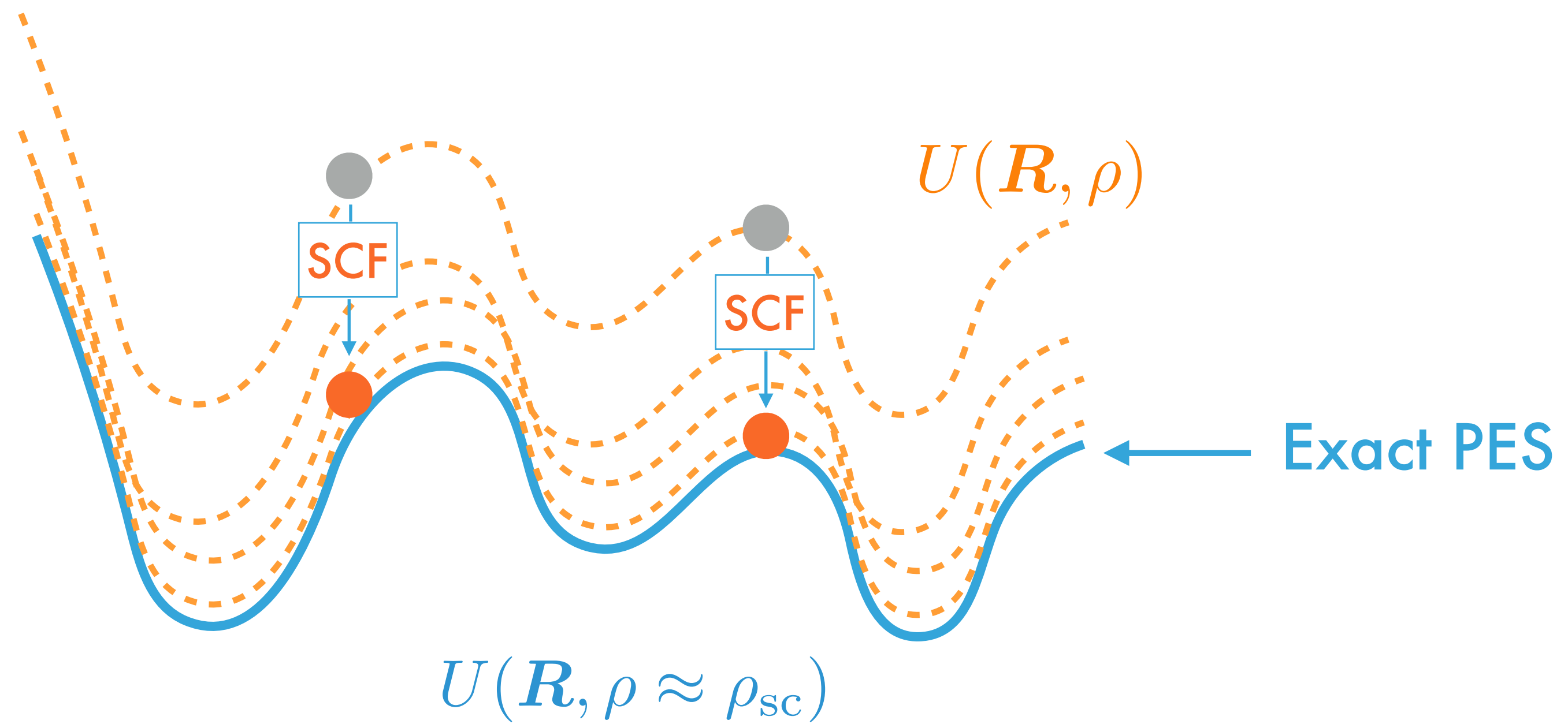


Main Concepts of Extended Lagrangian BOMD (XL-BOMD)

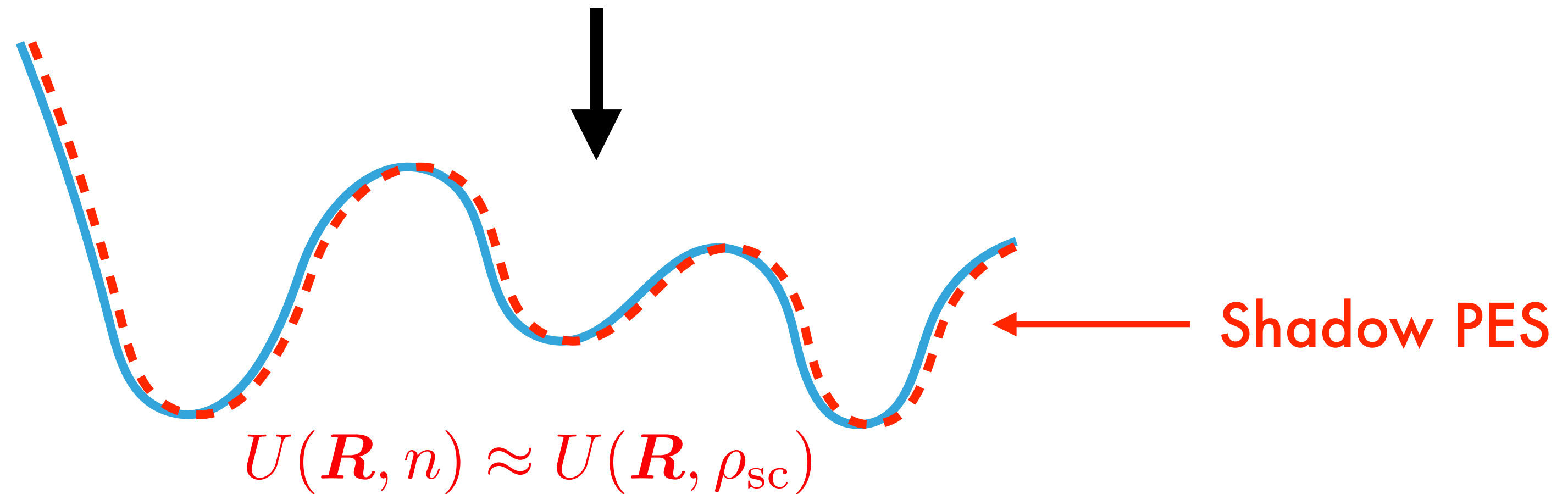


1. Introduction of Shadow PES for approximate density n

Sample the exact PES
with approximate forces



Treat an approximate
PES with exact forces



Linearize around constant auxiliary density n :

$$\mathcal{F}(\rho, n) = F[n] + \int \left. \frac{\partial F[\rho]}{\partial \rho(\mathbf{r})} \right|_{\rho=n} (\rho(\mathbf{r}) - n(\mathbf{r})) d\mathbf{r} = F[n] + \mathcal{O}[(\rho - n)^2]$$

Linearize around constant auxiliary density n :

$$\mathcal{F}(\rho, n) = F[n] + \int \left. \frac{\partial F[\rho]}{\partial \rho(\mathbf{r})} \right|_{\rho=n} (\rho(\mathbf{r}) - n(\mathbf{r})) d\mathbf{r} = F[n] + \mathcal{O}[(\rho - n)^2]$$
$$\mathcal{U}(\mathbf{R}, n) = \mathcal{F}[q[n], n] + \int v_{ext}(\mathbf{R}, \mathbf{r}) q[n](\mathbf{r}) d\mathbf{r} + V_{\text{nuc-nuc}}(\mathbf{R})$$

Linearize around constant auxiliary density n :

$$\mathcal{F}(\rho, n) = F[n] + \int \left. \frac{\partial F[\rho]}{\partial \rho(\mathbf{r})} \right|_{\rho=n} (\rho(\mathbf{r}) - n(\mathbf{r})) d\mathbf{r} = F[n] + \mathcal{O}[(\rho - n)^2]$$

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No SCF necessary!

$$H[n] \Psi_i = \epsilon_i \Psi_i$$

$$q[n] = \sum_{i \in \text{occ}} f_i |\Psi_i|^2$$

Linearize around constant auxiliary density n :

$$\mathcal{F}(\rho, n) = F[n] + \int \left. \frac{\partial F[\rho]}{\partial \rho(\mathbf{r})} \right|_{\rho=n} (\rho(\mathbf{r}) - n(\mathbf{r})) d\mathbf{r} = F[n] + \mathcal{O}[(\rho - n)^2]$$

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Error in the potential

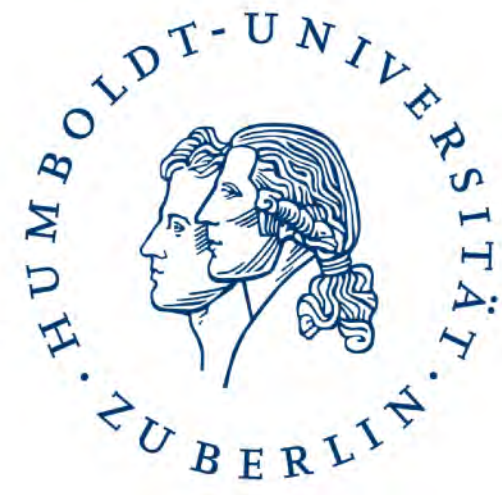
$$\mathcal{U}(\mathbf{R}, n) - U(\mathbf{R}) = \mathcal{O}((q[n] - n)^2)$$

Residual is measure for accuracy

No SCF necessary!

$$H[n] \Psi_i = \epsilon_i \Psi_i$$

$$q[n] = \sum_{i \in \text{occ}} f_i |\Psi_i|^2$$



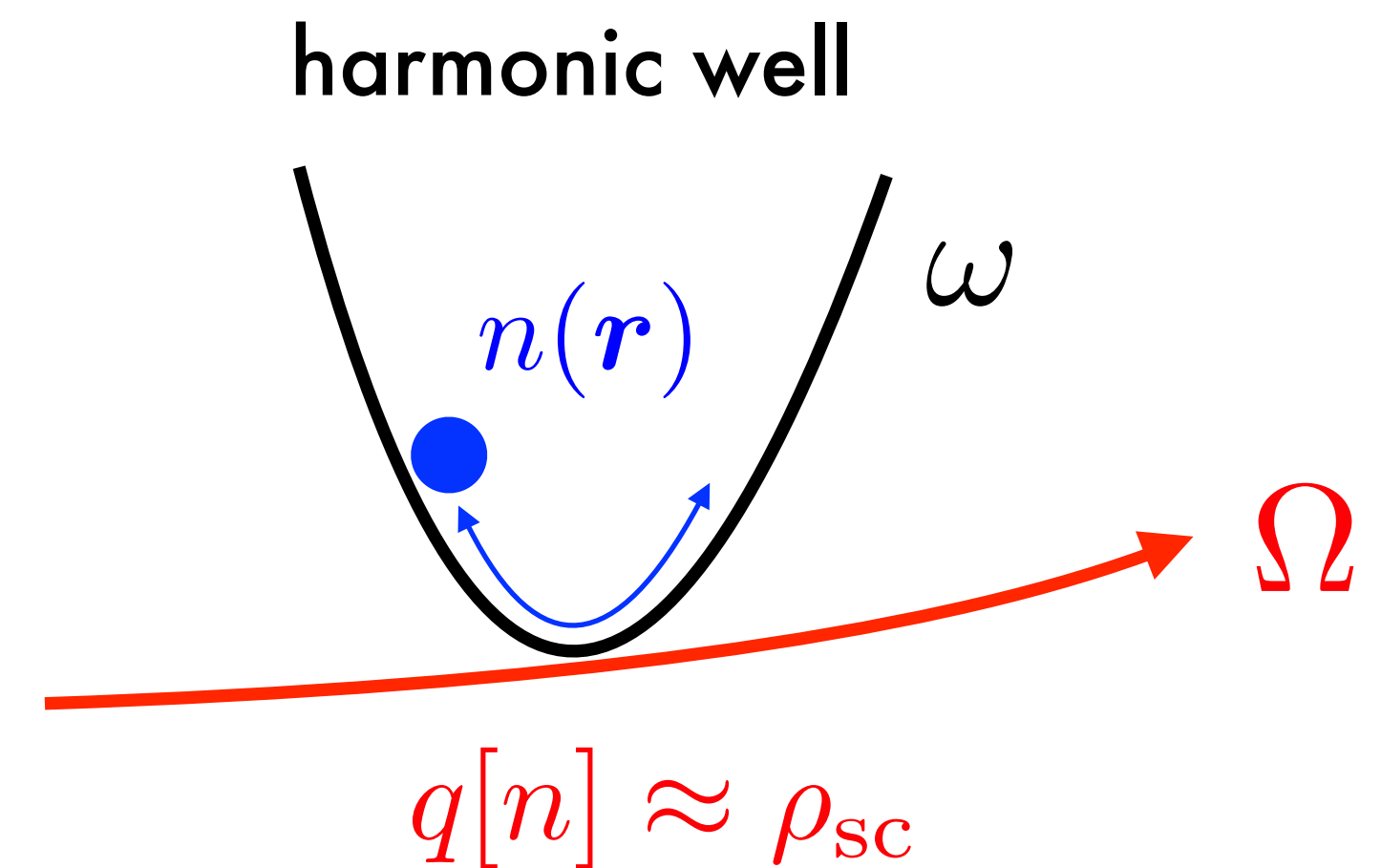
Main Concepts of XL-BOMD



$$\mathcal{L}(\mathbf{R}, \dot{\mathbf{R}}, n, \dot{n}) = \frac{1}{2} \sum_I M_I \dot{R}_I^2 - \mathcal{U}_{\text{BO}}(\mathbf{R}, n)$$

$$\mathcal{L}(\mathbf{R}, \dot{\mathbf{R}}, n, \dot{n}) = \frac{1}{2} \sum_I M_I \dot{R}_I^2 - \mathcal{U}_{\text{BO}}(\mathbf{R}, n) + \frac{\mu}{2} \int (\dot{n}(\mathbf{r}))^2 d\mathbf{r} - \frac{\mu\omega^2}{2} \int \int (q[n](\mathbf{r}) - n(\mathbf{r})) T(\mathbf{r}, \mathbf{r}') (q[n](\mathbf{r}') - n(\mathbf{r}')) d\mathbf{r} d\mathbf{r}'$$

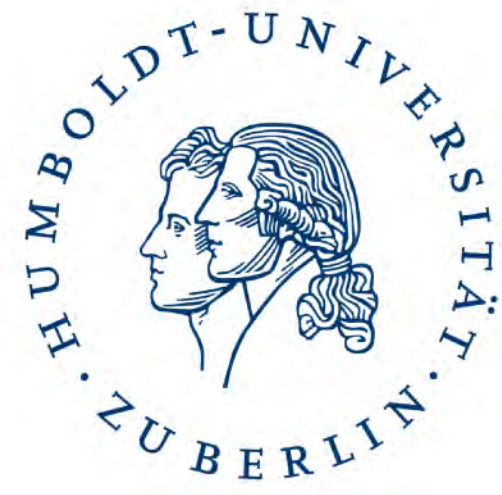
n is a dynamical field variable that evolves in a harmonic well around the ground state density $q[n]$





Main Concepts of XL-BOMD





Equations of Motion in Adiabatic Limit



Modified Leapfrog velocity-Verlet integration scheme

Electronic degrees of freedom

and

Nuclear degrees of freedom



Equations of Motion in Adiabatic Limit



Nuclear degrees of freedom

Standard leapfrog velocity Verlet scheme

Electronic degrees of freedom

$$n(t + \delta t) = 2n(t) - n(t - \delta t) + \delta t^2 \ddot{n}(t) + \alpha \sum_{k=0}^{k_{\max}} c_k n(t - k\delta t)$$

Electronic degrees of freedom

$$n(t + \delta t) = 2n(t) - n(t - \delta t) + \delta t^2 \ddot{n}(t) + \alpha \sum_{k=0}^{k_{\max}} c_k n(t - k\delta t)$$

Dissipation to remove noise

Electronic degrees of freedom

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Equation of motion

$$\ddot{n}(\mathbf{r}) = -\omega^2 K(q[n](\mathbf{r}) - n(\mathbf{r}))$$

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Scaled delta kernel approximation

$$K = -c \delta(\mathbf{r} - \mathbf{r}'), c \in [0, 1]$$

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Equation of motion

$$\ddot{n}(\mathbf{r}) = -\omega^2 \mathbf{K}(q[n](\mathbf{r}) - n(\mathbf{r}))$$

Scaled delta kernel approximation

$$\mathbf{K} = -c \delta(\mathbf{r} - \mathbf{r}'), \quad c \in [0, 1]$$

Constant of motion

$$E_{\text{tot}} = \frac{1}{2} \sum_I M_I \dot{R}_I^2 + \mathcal{U}(\mathbf{R}, n)$$

Residual as measure of accuracy

$$(q[n] - n) \sim \delta t^2$$

What is actually done?

The auxiliary electronic system can be described by density, density matrix, ...

The electron density in FHI-aims is a grid-based quantity

- ▶ High memory demand
- ▶ Can change upon geometry update

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The auxiliary electronic system can be described by density, density matrix, ...

We are using the density matrix D for the integration

- ▶ Memory determined by basis set
- ▶ Calculated by default in FHI-aims (except for small molecules)

$$n(\mathbf{r}) = \sum_{i,j} \phi_i(\mathbf{r}) D_{ij} \phi_j(\mathbf{r})$$

$$q(\mathbf{r}) = \sum_{i,j} \phi_i(\mathbf{r}) P_{ij} \phi_j(\mathbf{r})$$

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$$D(t + \delta t) = 2D(t) - D(t - \delta t) + \delta t^2 \ddot{D}(t) + \alpha \sum_{k=0}^{k_{\max}} c_k D(t - k\delta t)$$

Equation of motion

$$\ddot{D}(t) = -\omega^2 c (P[D] - D)$$

Residual

$$(P[D] - D) \sim \delta t^2$$



- ▶ Electronic structure problem is handled by FHI-aims [1,2]
- ▶ All-electron framework with numeric atom-centered orbitals

Electronic Structure Infrastructure

- ▶ Additional integration of auxiliary electronic system is implemented in ELSI [3]
- ▶ Full ScaLAPACK support
- ▶ Allows for integration in other electronic structure codes

[1] V. Blum *et al.*, *Comput. Phys. Commun.* **180**, 2175 (2009).

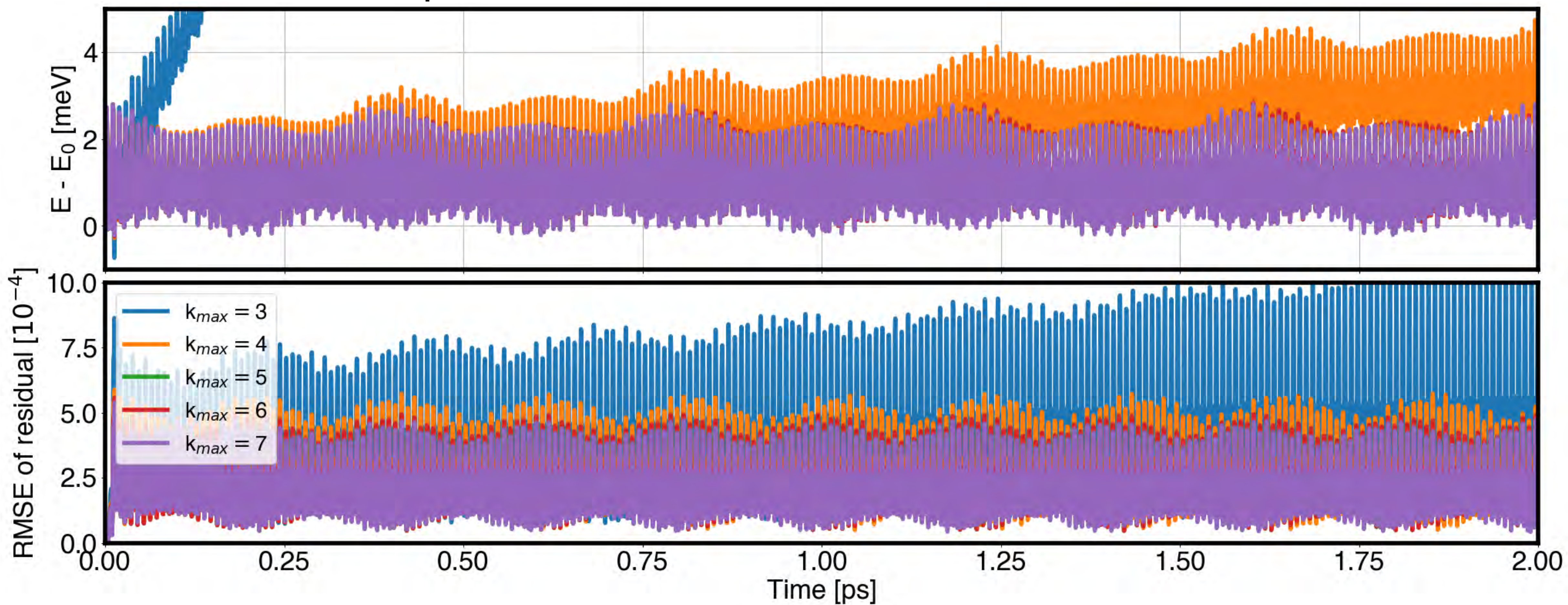
[2] V. Havu *et al.*, *J. Comput. Phys.* **228**, 8367 (2009).

[3] V. Yu *et al.*, *Comput. Phys. Commun.* **256**, 107459 (2020).

Impact of Dissipation for H₂O Molecule at 300 K

$$n(t + \delta t) = 2n(t) - n(t - \delta t) + \delta t^2 \ddot{n}(t) + \alpha \sum_{k=0}^{k_{\max}} c_k n(t - k\delta t)$$

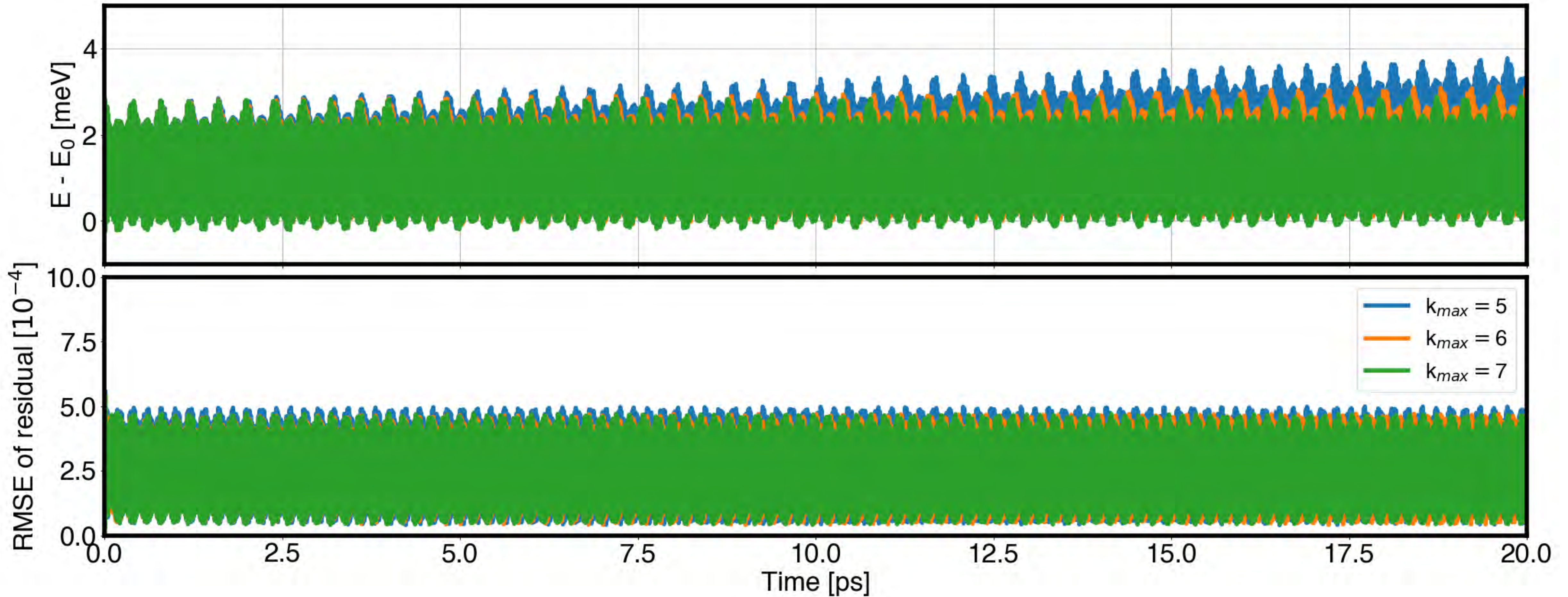
$c=0.6$, 0.4 fs timestep

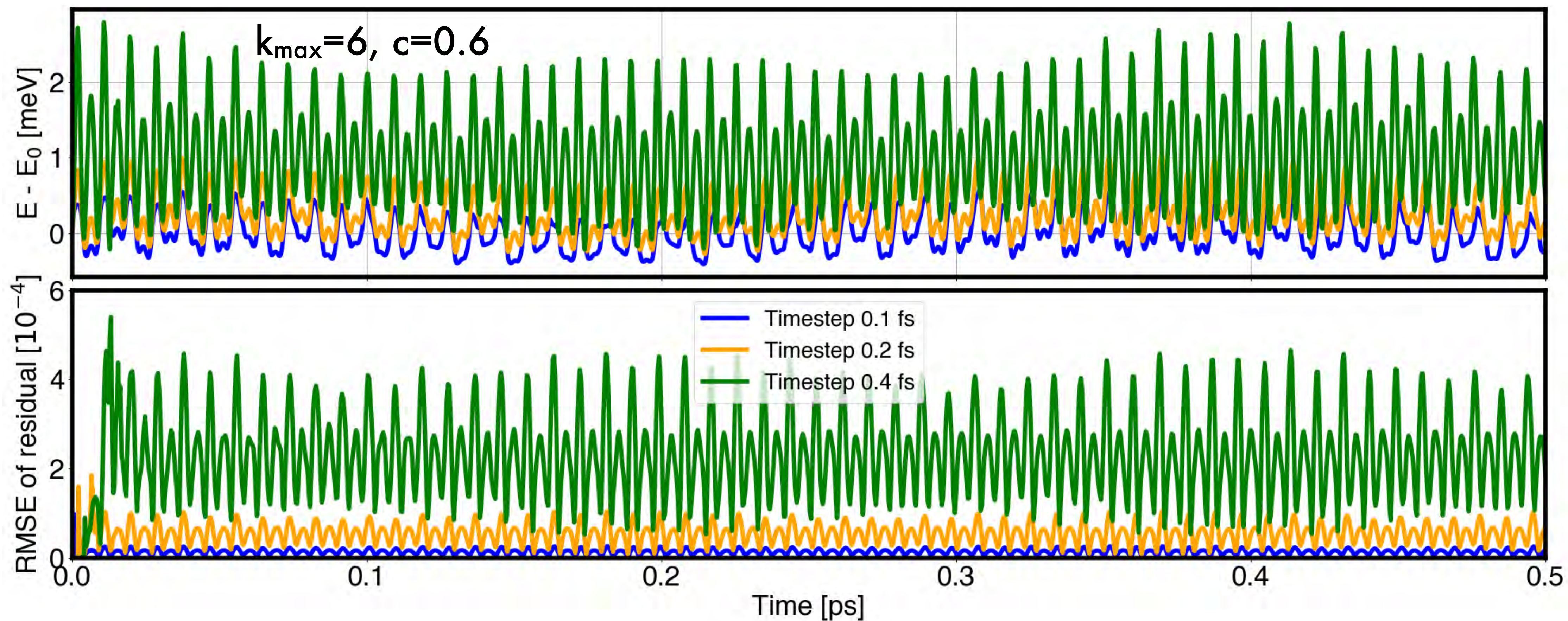


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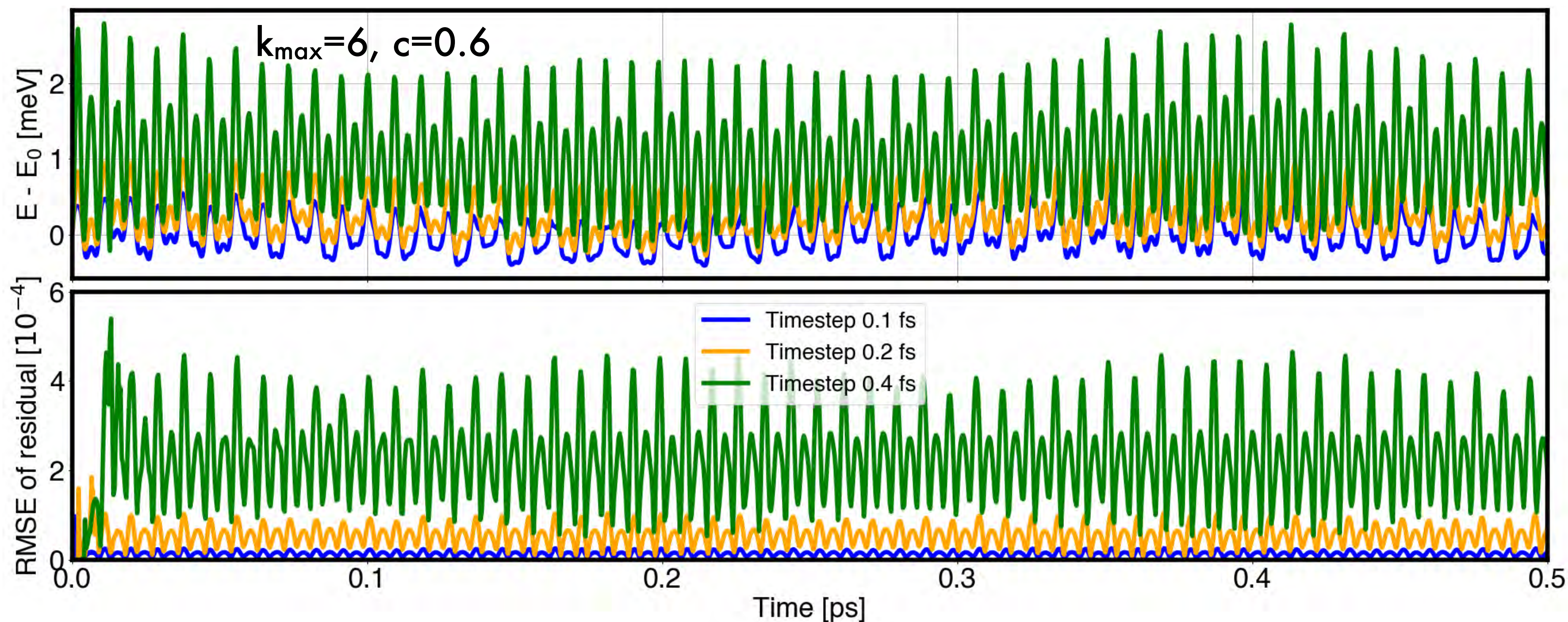


Impact of Timestep for the H₂O Molecule at 300 K

Ratio of residuals over last 0.1 ps:
 $(q[n] - n)$

0.1 fs → 0.2fs	0.2 fs → 0.4fs
4.0	4.4

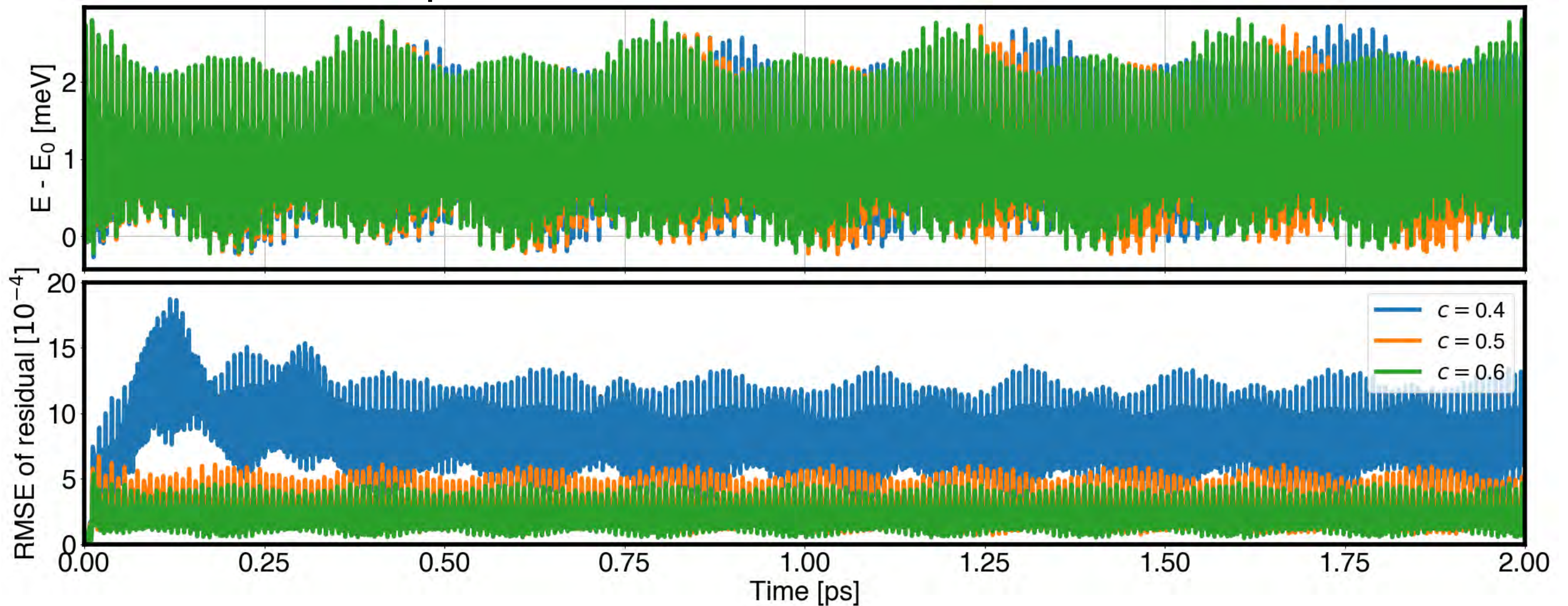
Residual scales as $\sim \delta t^2$



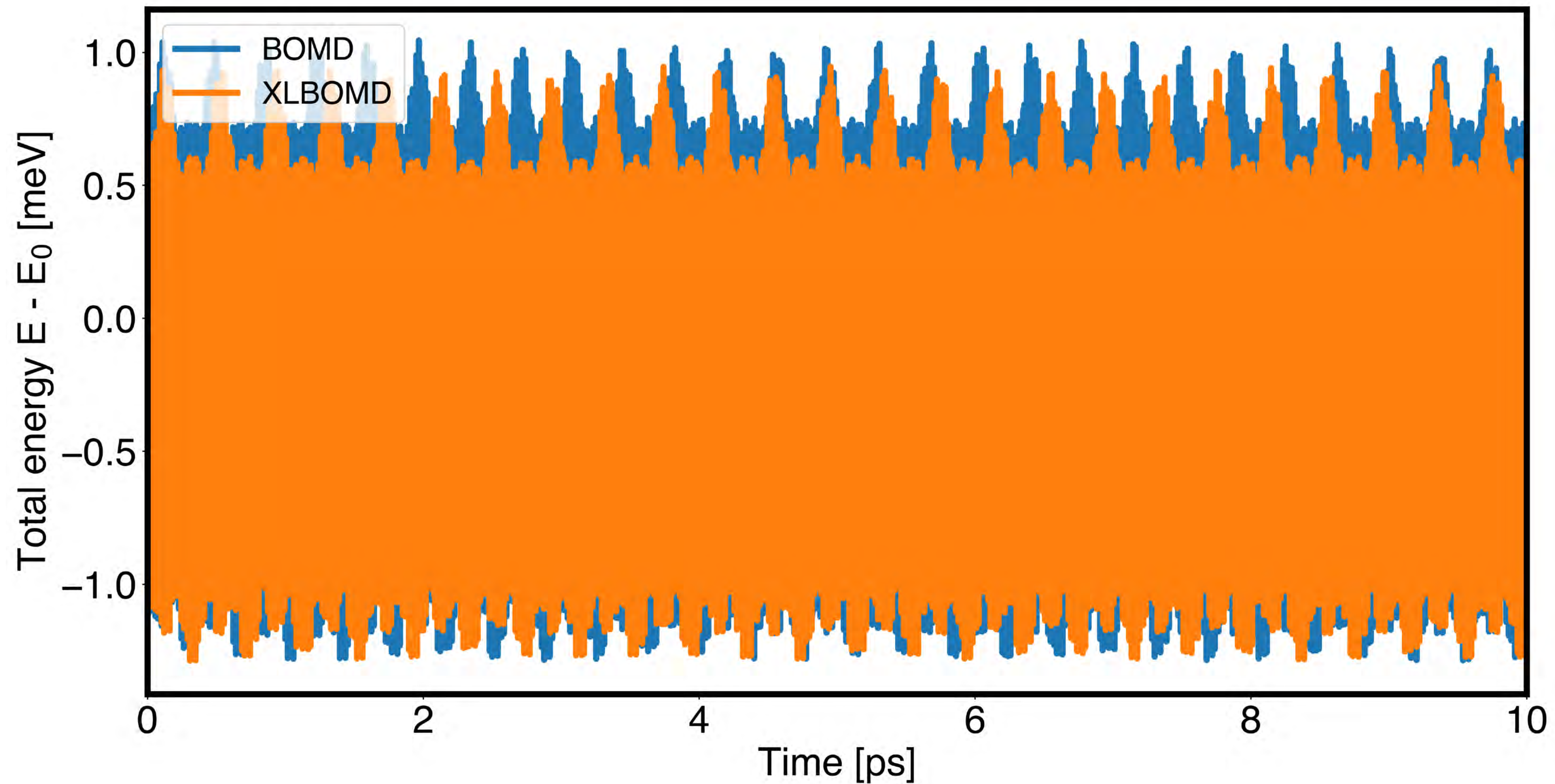
Impact of Delta Parameter for the H₂O Molecule at 300 K

$$K = -c\delta(\mathbf{r} - \mathbf{r}'), c \in [0, 1] \quad \longrightarrow \quad \ddot{n}(\mathbf{r}) = -\omega^2 K(q[n](\mathbf{r}) - n(\mathbf{r}))$$

$k_{\max}=6$, 0.4 fs timestep

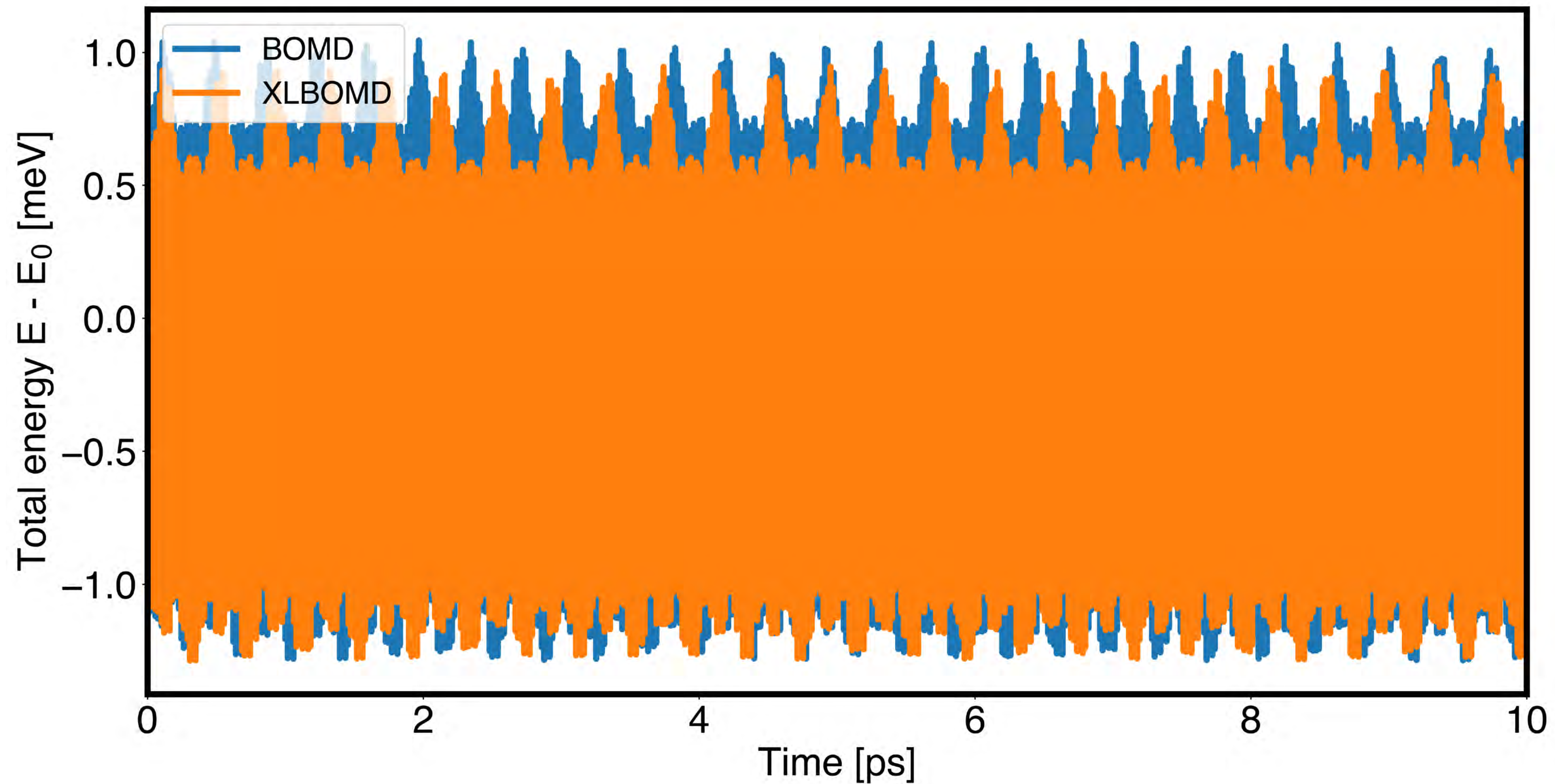


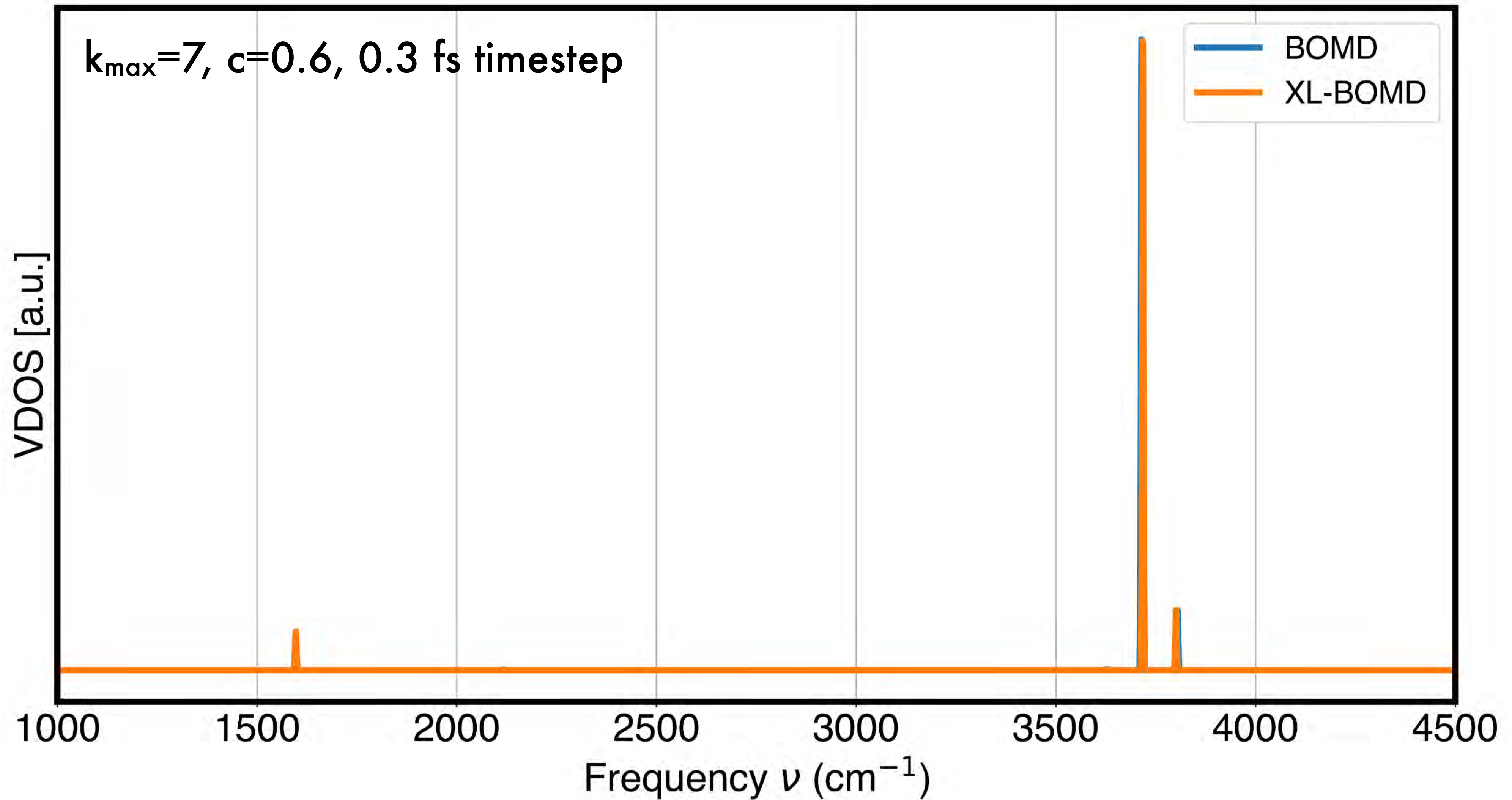
$k_{\max}=7$, $c=0.6$, 0.3 fs timestep



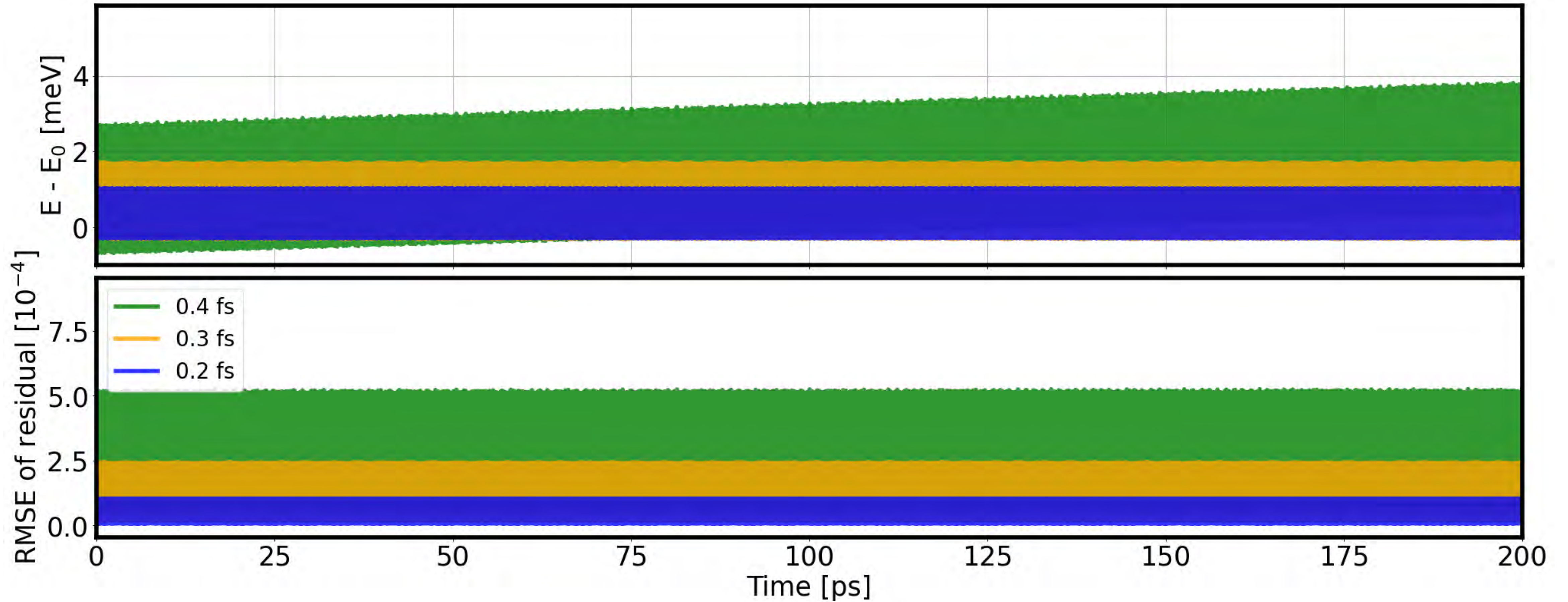
Speedup of 3

$k_{\max}=7$, $c=0.6$, 0.3 fs timestep





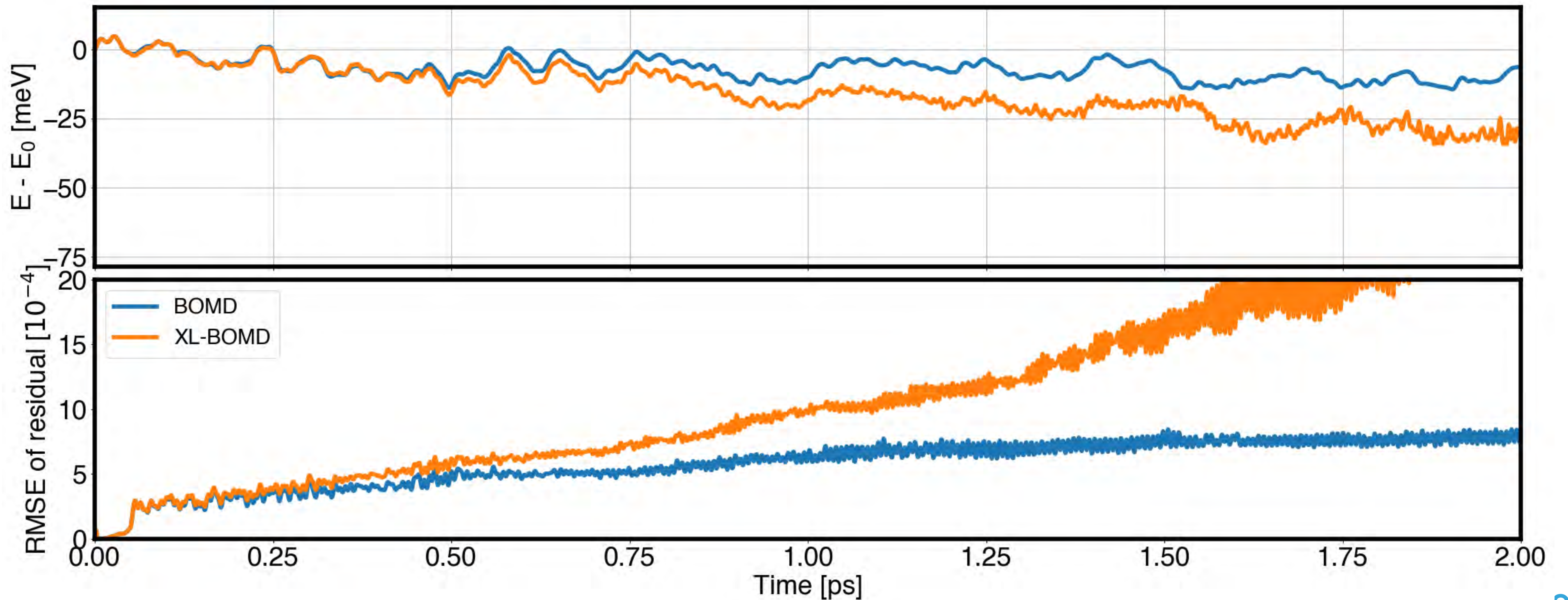
$k_{\max}=7, c=0.6$



What doesn't work at the moment?

Simulations for actual solids don't behave as expected ...

Ga_2O_3 bulk, 1 fs timestep, $c=0.1$, $k_{\text{max}}=7$



Thank you for your attention!