CyberTraining project:

Implementing a numerical efficient formulation of FSSH in Libra

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Agenda

- Motivation & Goal
- Formulation of a new hop probability
- Numerical experiment
- Time & workflow overview

Motivation & Goal

Motivation: issues of the time step size Δt for dynamics

Small Δt

$\Downarrow$

longer running time

Δt issues

When to trust Δt?

How to choose Δt?

Motivation: FSSH procedure from time t to $t + \Delta t$

1) Propagate classical coordinates from t to $t + \Delta t$ at active state m:

$$\boxed{\begin{aligned} \dot{\boldsymbol{x}} &= \boldsymbol{p} \\ \dot{\boldsymbol{p}} &= \boldsymbol{F}_{\boldsymbol{m}}^{\boldsymbol{adi}}(\boldsymbol{x}) \end{aligned}}$$

2) Propagate TDSE of the electronic amplitudes from t to $t + \Delta t$:

$$\boxed{\boldsymbol{i\varepsilon\dot{c}^{adi}(t) = H^{adi}(t)c^{adi}(t)}}$$

with $\boldsymbol{H_{m,n}^{adi}(t) = \delta_{m,n}E_m(x) - i\varepsilon d^{m,n}(x)^T p}$

3) Hop to state n with probability:

$$\boxed{\boldsymbol{P_{m,n}^{FSSH}(t, t + \Delta t) = \frac{2\Delta t\, Re\left(\rho_{n,m}^{adi}\right) d^{m,n}(x)^T p}{\rho_{m,m}^{adi}}}}$$

with $\boldsymbol{\rho_{n,m}^{adi} = c_n^{adi}\overline{c_m^{adi}}}$

Issue: energy conservation is not enough as indicator

1) Propagate classical coordinates from t to $t + \Delta t$ at active state m:

$$\boxed{\begin{aligned} \dot{\boldsymbol{x}} &= \boldsymbol{p} \\ \dot{\boldsymbol{p}} &= \boldsymbol{F}_{\boldsymbol{m}}^{\boldsymbol{adi}}(\boldsymbol{x}) \end{aligned}}$$

2) Propagate TDSE of the electronic amplitudes from t to $t + \Delta t$:

$$\boxed{\boldsymbol{i\varepsilon\dot{c}^{adi}(t) = H^{adi}(t)c^{adi}(t)}}$$

with $\boldsymbol{H_{m,n}^{adi}(t) = \delta_{m,n}E_m(x) - i\varepsilon d^{m,n}(x)^T p}$

3) Hop to state n with probability:

$$\boxed{\boldsymbol{P_{m,n}^{FSSH}(t, t + \Delta t) = \frac{2\Delta t\, Re\left(\rho_{n,m}^{adi}\right) d^{m,n}(x)^T p}{\rho_{m,m}^{adi}}}}$$

with $\boldsymbol{\rho_{n,m}^{adi} = c_n^{adi}\overline{c_m^{adi}}}$

Energy conservation only indicates how well step 1) is propagated but is no indicator of the convergence of the other steps.

Issue: typical time step size hierarchy

1) Propagate classical coordinates from t to $t + \Delta t$ at active state m:

$$\boxed{\begin{aligned} \dot{\boldsymbol{x}} &= \boldsymbol{p} \\ \dot{\boldsymbol{p}} &= \boldsymbol{F}_{\boldsymbol{m}}^{\boldsymbol{adi}}(\boldsymbol{x}) \end{aligned}}$$

2) Propagate TDSE of the electronic amplitudes from t to $t + \Delta t$:

$$\boxed{\boldsymbol{i\varepsilon\dot{c}^{adi}(t) = H^{adi}(t)c^{adi}(t)}}$$

with $\boldsymbol{H_{m,n}^{adi}(t) = \delta_{m,n}E_m(x) - i\varepsilon \boxed{d^{m,n}(x)}^T p}$

3) Hop to state n with probability:

$$\boxed{\boldsymbol{P_{m,n}^{FSSH}(t, t + \Delta t) = \frac{2\Delta t\, Re\left(\rho_{n,m}^{adi}\right)\boxed{d^{m,n}(x)}^T p}{\rho_{m,m}^{adi}}}}$$

with $\boldsymbol{\rho_{n,m}^{adi} = c_n^{adi}\overline{c_m^{adi}}}$

Step 2) and 3) lead to decreasing Δt due to the exploding behavior of $d^{m,n}$ at intersections

$\boldsymbol{\Delta t}$

General Goal

Find numerical efficient formulations and methods of step 2) and 3) such that:

- **FSSH boosts up and converges faster**
- **Step 2) and 3) become less sensitive then step 1)**
- **Energy conservation can be used as a convergence indicator for FSSH**

Goal of this particular presentation

1) Propagate classical coordinates from t to $t + \Delta t$ at active state m:

$$\dot{x} = p$$
$$\dot{p} = F_m^{adi}(x)$$

2) Propagate TDSE of the electronic amplitudes from t to $t + \Delta t$:

$$i\varepsilon\dot{c}^{adi}(t) = H^{adi}(t)c^{adi}(t)$$

with $H_{m,n}^{adi}(t) = \delta_{m,n}E_m(x) - i\varepsilon d^{m,n}(x)^T p$

Find a numerical efficient formulation of $P_{m,n}^{FSSH}$

3) Hop to state n with probability:

$$P_{m,n}^{FSSH}(t, t + \Delta t) = \frac{2\Delta t\, Re\left(\rho_{n,m}^{adi}\right) d^{m,n}(x)^T p}{\rho_{m,m}^{adi}}$$

with $\rho_{n,m}^{adi} = c_n^{adi}\overline{c_m^{adi}}$

Formulation of a new hop probability

Derivation of the hop probability

$$\boxed{\boldsymbol{P_{m,out}(t, t+\Delta t) = \frac{\rho_{m,m}^{adi}(t) - \rho_{m,m}^{adi}(t+\Delta t)}{\rho_{m,m}^{adi}(t)}}}$$

Derivation of the hop probability: FSSH (1/3)

FSSH

$$P_{m,out}(t, t+\Delta t) = \frac{\rho_{m,m}^{adi}(t) - \rho_{m,m}^{adi}(t+\Delta t)}{\rho_{m,m}^{adi}(t)}$$

$$\frac{\rho_{m,m}^{adi}(t) - \rho_{m,m}^{adi}(t+\Delta t)}{\rho_{m,m}^{adi}(t)} \underset{\text{FEM}}{\approx} \frac{\dot{\rho}_{m,m}^{adi}(t)\,\Delta t}{\rho_{m,m}^{adi}(t)}$$

Derivation of the hop probability: FSSH (2/3)

FSSH

$$P_{m,out}(t, t+\Delta t) = \frac{\rho_{m,m}^{adi}(t) - \rho_{m,m}^{adi}(t+\Delta t)}{\rho_{m,m}^{adi}(t)}$$

$$\frac{\rho_{m,m}^{adi}(t) - \rho_{m,m}^{adi}(t+\Delta t)}{\rho_{m,m}^{adi}(t)} \underset{\text{FEM}}{\approx} \frac{\dot{\rho}_{m,m}^{adi}(t)\,\Delta t}{\rho_{m,m}^{adi}(t)}$$

$$\frac{\dot{\rho}_{m,m}^{adi}(t)\,\Delta t}{\rho_{m,m}^{adi}(t)} = \sum_{n \neq m} \frac{2\Delta t\, Re\left(\rho_{n,m}^{adi}\right) d^{m,n}(x)^T p}{\rho_{m,m}^{adi}}$$

Derivation of the hop probability: FSSH (3/3)

FSSH

$$P_{m,out}(t, t+\Delta t) = \frac{\rho_{m,m}^{adi}(t) - \rho_{m,m}^{adi}(t+\Delta t)}{\rho_{m,m}^{adi}(t)}$$

$$\frac{\rho_{m,m}^{adi}(t) - \rho_{m,m}^{adi}(t+\Delta t)}{\rho_{m,m}^{adi}(t)} \underset{\text{FEM}}{\approx} \frac{\dot{\rho}_{m,m}^{adi}(t)\,\Delta t}{\rho_{m,m}^{adi}(t)}$$

$$\frac{\dot{\rho}_{m,m}^{adi}(t)\,\Delta t}{\rho_{m,m}^{adi}(t)} = \sum_{n \neq m} \frac{2\Delta t\, Re\left(\rho_{n,m}^{adi}\right) d^{m,n}(x)^T p}{\rho_{m,m}^{adi}}$$

$$P_{m,out} \overset{!}{=} \sum_{n \neq m} P_{m,n}$$

$$P_{m,n}^{FSSH}(t, t+\Delta t) := \frac{2\Delta t\, Re\left(\rho_{n,m}^{adi}\right) d^{m,n}(x)^T p}{\rho_{m,m}^{adi}}$$

Derivation of the hop probability: FSSH2 (1/3)

FSSH

$$P_{m,out}(t, t+\Delta t) = \frac{\rho^{adi}_{m,m}(t) - \rho^{adi}_{m,m}(t+\Delta t)}{\rho^{adi}_{m,m}(t)}$$

$$\frac{\rho^{adi}_{m,m}(t) - \rho^{adi}_{m,m}(t+\Delta t)}{\rho^{adi}_{m,m}(t)} \underset{\text{FEM}}{\approx} \frac{\dot{\rho}^{adi}_{m,m}(t)\,\Delta t}{\rho^{adi}_{m,m}(t)}$$

$$\frac{\dot{\rho}^{adi}_{m,m}(t)\,\Delta t}{\rho^{adi}_{m,m}(t)} = \sum_{n \neq m} \frac{2\Delta t\, Re\left(\rho^{adi}_{n,m}\right) d^{m,n}(x)^T p}{\rho^{adi}_{m,m}}$$

$$P_{m,out} \overset{!}{=} \sum_{n \neq m} P_{m,n}$$

$$P^{FSSH}_{m,n}(t, t+\Delta t) := \frac{2\Delta t\, Re\left(\rho^{adi}_{n,m}\right) d^{m,n}(x)^T p}{\rho^{adi}_{m,m}}$$

FSSH2

$$\sum_{n} \rho^{adi}_{n,n}(t) = 1 \Leftrightarrow \rho^{adi}_{m,m}(t) = 1 - \sum_{n \neq m} \rho^{adi}_{n,n}(t)$$

Derivation of the hop probability: FSSH2 (2/3)

FSSH

$$P_{m,out}(t, t+\Delta t) = \frac{\rho^{adi}_{m,m}(t) - \rho^{adi}_{m,m}(t+\Delta t)}{\rho^{adi}_{m,m}(t)}$$

$$\frac{\rho^{adi}_{m,m}(t) - \rho^{adi}_{m,m}(t+\Delta t)}{\rho^{adi}_{m,m}(t)} \underset{\text{FEM}}{\approx} \frac{\dot{\rho}^{adi}_{m,m}(t)\,\Delta t}{\rho^{adi}_{m,m}(t)}$$

$$\frac{\dot{\rho}^{adi}_{m,m}(t)\,\Delta t}{\rho^{adi}_{m,m}(t)} = \sum_{n \neq m} \frac{2\Delta t\, Re\left(\rho^{adi}_{n,m}\right) d^{m,n}(x)^T p}{\rho^{adi}_{m,m}}$$

$$P_{m,out} \overset{!}{=} \sum_{n \neq m} P_{m,n}$$

$$P^{FSSH}_{m,n}(t, t+\Delta t) := \frac{2\Delta t\, Re\left(\rho^{adi}_{n,m}\right) d^{m,n}(x)^T p}{\rho^{adi}_{m,m}}$$

FSSH2

$$\sum_{n} \rho^{adi}_{n,n}(t) = 1 \Leftrightarrow \rho^{adi}_{m,m}(t) = 1 - \sum_{n \neq m} \rho^{adi}_{n,n}(t)$$

$$\frac{\rho^{adi}_{m,m}(t) - \rho^{adi}_{m,m}(t+\Delta t)}{\rho^{adi}_{m,m}(t)} = \sum_{n \neq m} \frac{\rho^{adi}_{n,n}(t+\Delta t) - \rho^{adi}_{n,n}(t)}{\rho^{adi}_{m,m}(t)}$$

Derivation of the hop probability: FSSH2 (3/3)

$$P_{m,out}(t, t+\Delta t) = \frac{\rho^{adi}_{m,m}(t) - \rho^{adi}_{m,m}(t+\Delta t)}{\rho^{adi}_{m,m}(t)}$$

FSSH

$$\frac{\rho^{adi}_{m,m}(t) - \rho^{adi}_{m,m}(t+\Delta t)}{\rho^{adi}_{m,m}(t)} \underset{\text{FEM}}{\approx} \frac{\dot{\rho}^{adi}_{m,m}(t)\,\Delta t}{\rho^{adi}_{m,m}(t)}$$

$$\frac{\dot{\rho}^{adi}_{m,m}(t)\,\Delta t}{\rho^{adi}_{m,m}(t)} = \sum_{n\neq m} \frac{2\Delta t\, Re\left(\rho^{adi}_{n,m}\right) d^{m,n}(x)^T p}{\rho^{adi}_{m,m}}$$

$$P_{m,out} \overset{!}{=} \sum_{n\neq m} P_{m,n}$$

$$P^{FSSH}_{m,n}(t, t+\Delta t) := \frac{2\Delta t\, Re\left(\rho^{adi}_{n,m}\right) d^{m,n}(x)^T p}{\rho^{adi}_{m,m}}$$

FSSH2

$$\sum_{n} \rho^{adi}_{n,n}(t) = 1 \Leftrightarrow \rho^{adi}_{m,m}(t) = 1 - \sum_{n\neq m} \rho^{adi}_{n,n}(t)$$

$$\frac{\rho^{adi}_{m,m}(t) - \rho^{adi}_{m,m}(t+\Delta t)}{\rho^{adi}_{m,m}(t)} = \sum_{n\neq m} \frac{\rho^{adi}_{n,n}(t+\Delta t) - \rho^{adi}_{n,n}(t)}{\rho^{adi}_{m,m}(t)}$$

$$P_{m,out} \overset{!}{=} \sum_{n\neq m} P_{m,n}$$

$$P^{FSSH2}_{m,n}(t, t+\Delta t) := \frac{\rho^{adi}_{n,n}(t+\Delta t) - \rho^{adi}_{n,n}(t)}{\rho^{adi}_{m,m}(t)}$$

Theoretical advantages of FSSH2 over FSSH

$$P_{m,n}^{FSSH}(t, t+\Delta t) := \frac{2\Delta t\, Re\left(\rho_{n,m}^{adi}\right) d^{m,n}(x)^T p}{\rho_{m,m}^{adi}}$$

vs.

$$P_{m,n}^{FSSH2}(t, t+\Delta t) := \frac{\rho_{n,n}^{adi}(t+\Delta t) - \rho_{n,n}^{adi}(t)}{\rho_{m,m}^{adi}(t)}$$

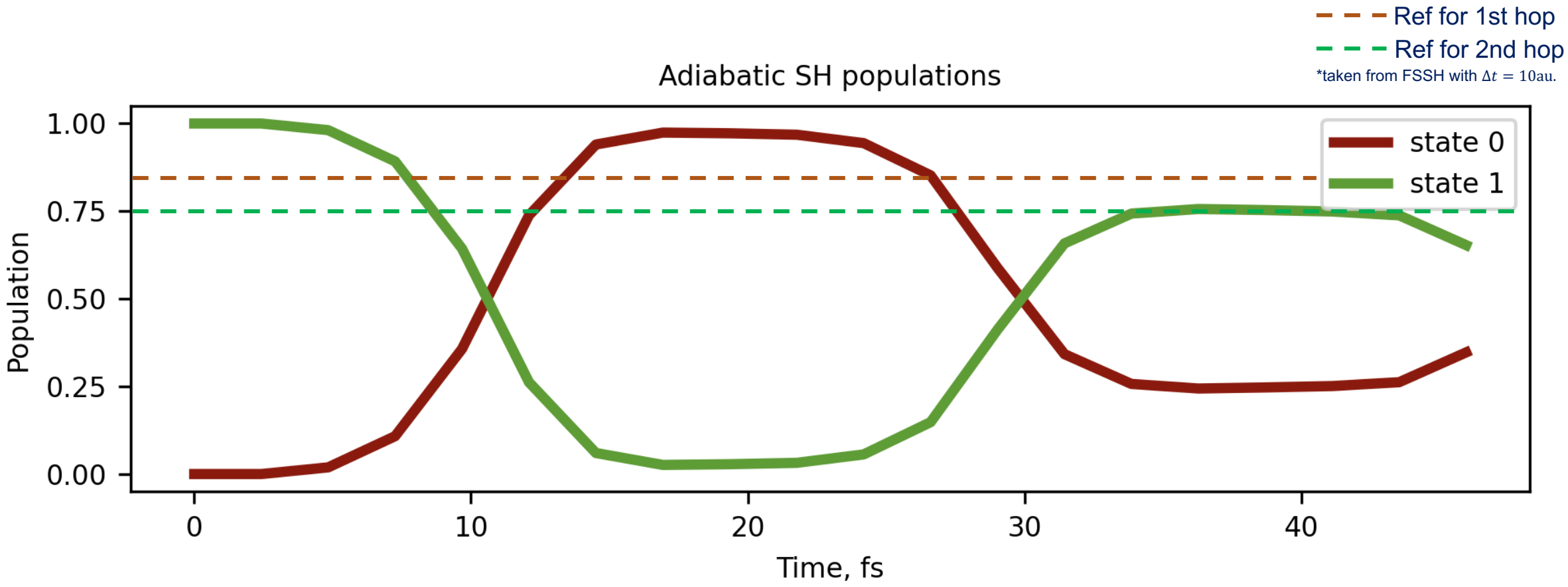
- **Numerical stable probability formula**
- **For a total of only two electronic states, we have** $P_{m,n}^{FSSH2} = P_{m,out} \overset{\text{FEM}}{\approx} P_{m,n}^{FSSH}$
- **FSSH2 can handle trivial crossings (depending on the TDSE propagator)**

Numerical experiment

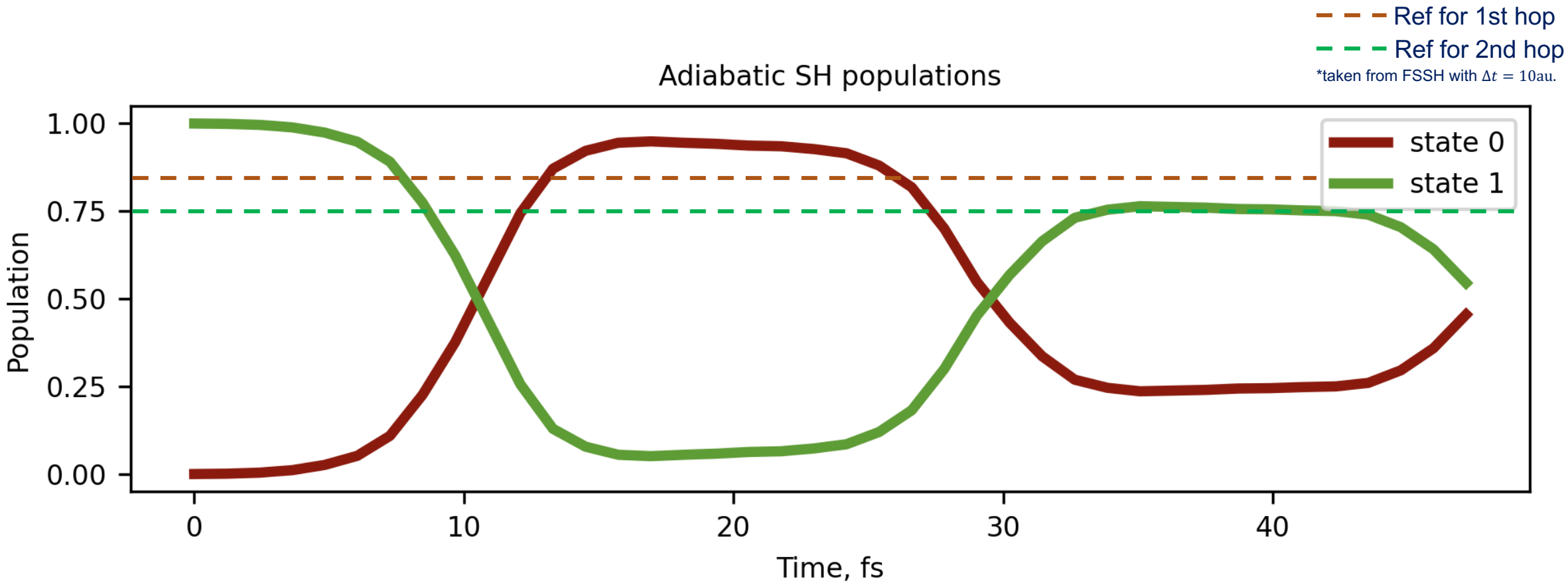
Input

- **Model:** Holstein model
- **Model parameters:** model_params3, as in the Tutorials of Libra
- **Simulation time:** 2000au. / ca. 50fs
- **Time step sizes Δt in au:** 100, 50, 20, 10
- **Methods:** FSSH, FSSH2, and GFSH (for Alexey)
- **Number of trajectories:** 1000 (5000 would be better to observe fewer deviations – but longer running time)

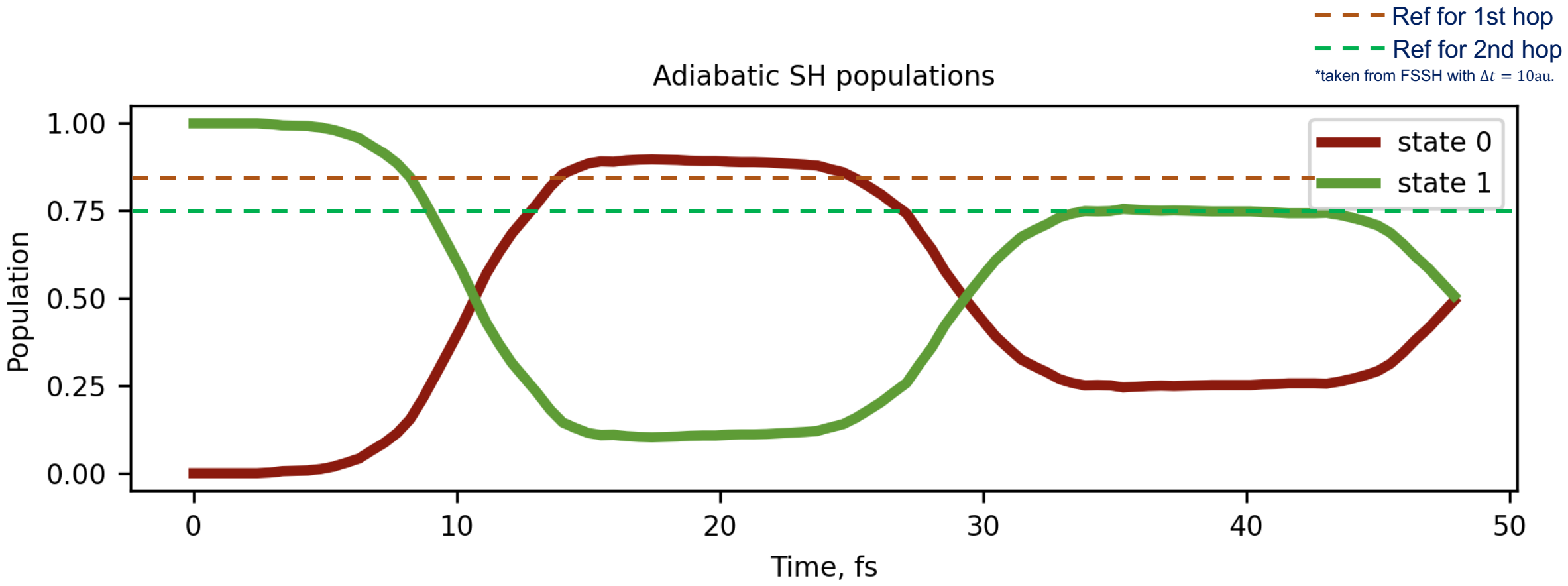
FSSH – $\Delta t = 100\text{au}$



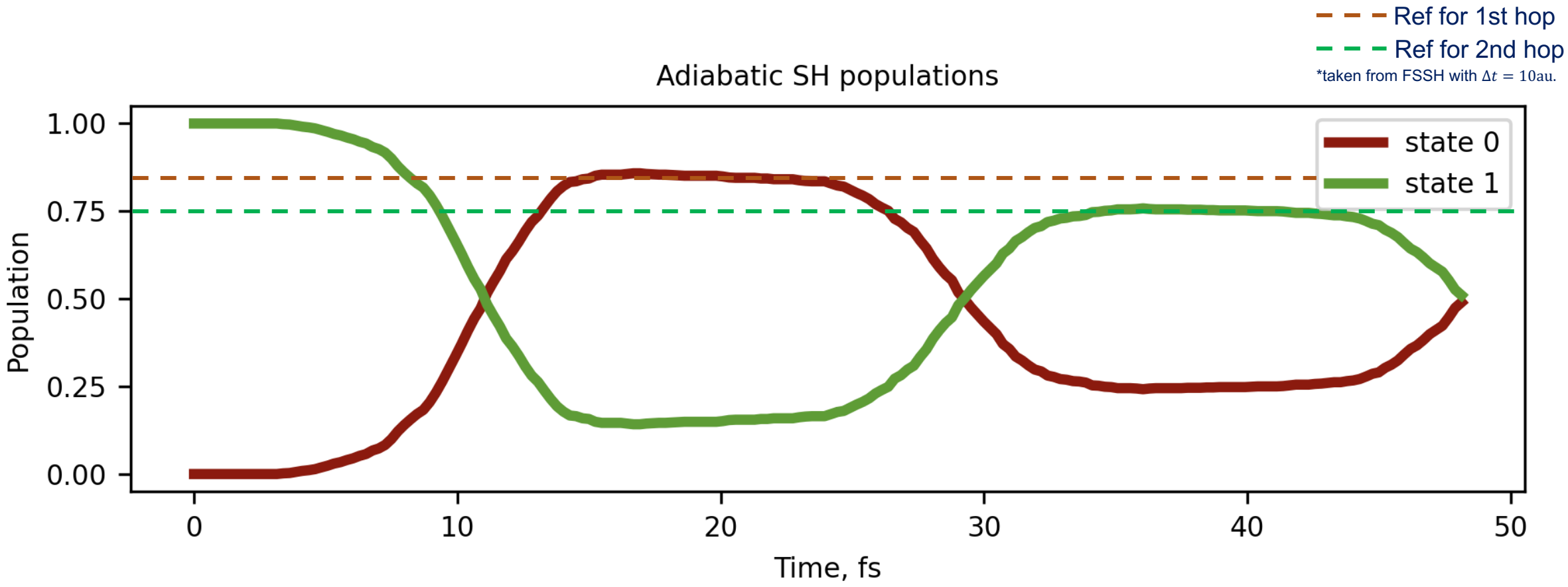
FSSH – $\Delta t = 50\text{au}$



FSSH – $\Delta t = 20\text{au}$

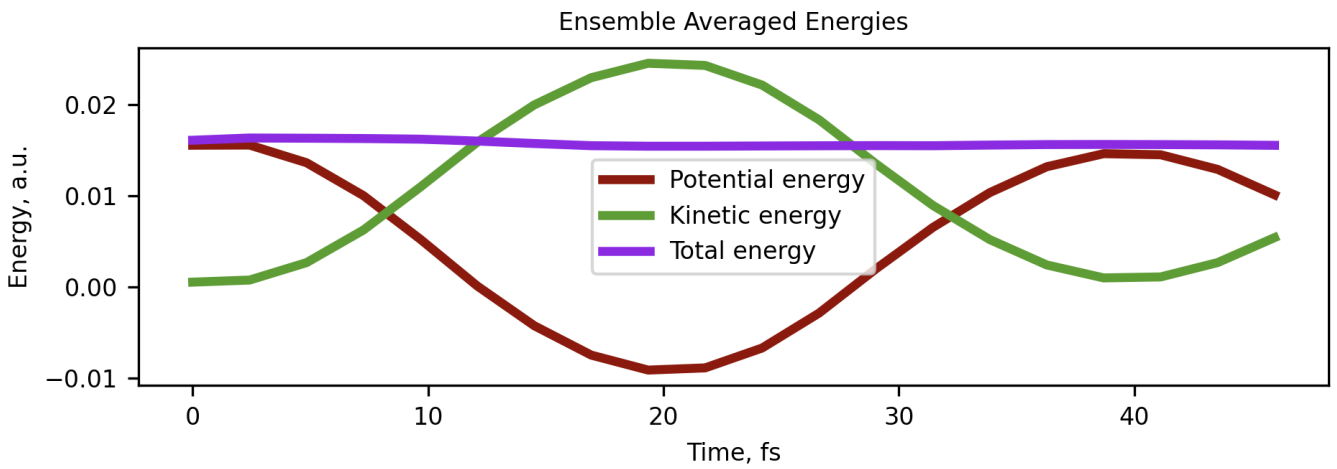


FSSH – $\Delta t = 10\text{au}$

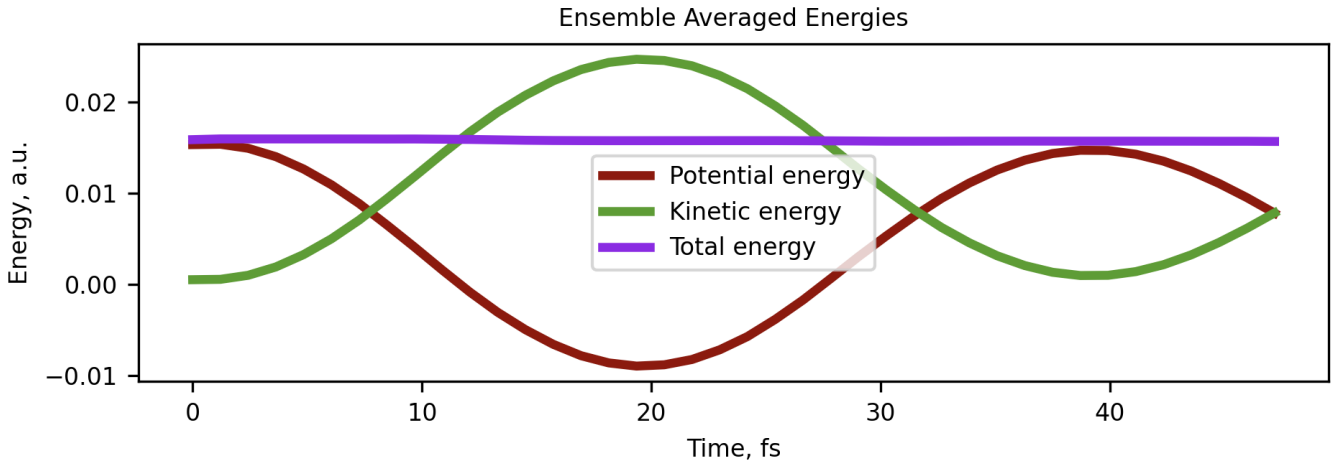


FSSH – energy conservation

$\Delta t = 100$:



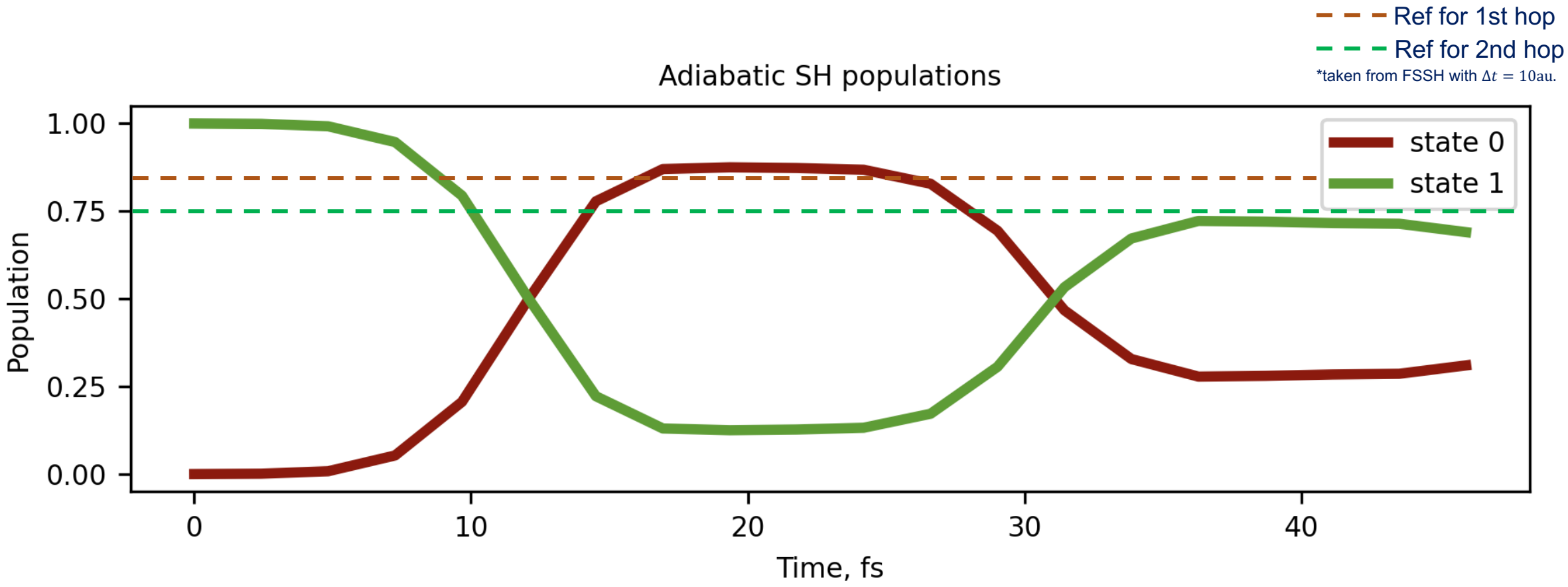
$\Delta t = 50$:



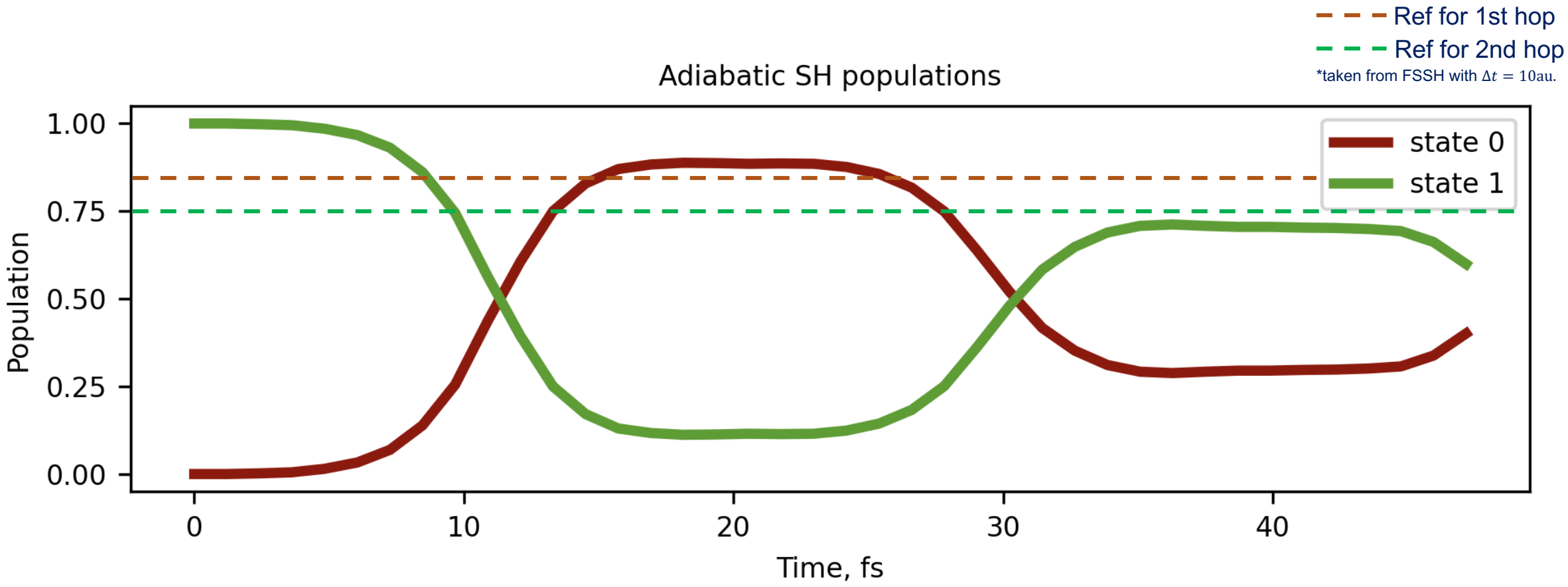
FSSH – observations

- Energy was already conserved at $\Delta t = 100\mathrm{au}$.
- However, FSSH started only to converge at around $\Delta t = 10 \text{ to } 20\mathrm{au}$.

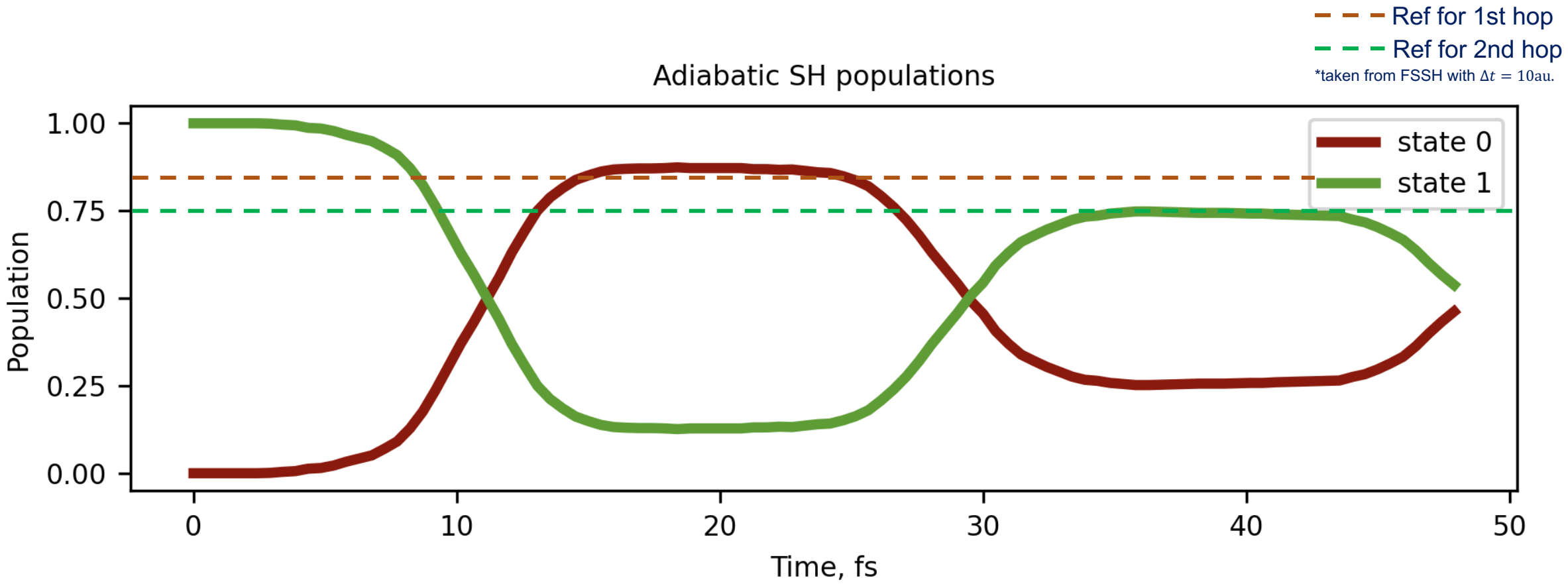
FSSH2 – $\Delta t = 100\text{au}$



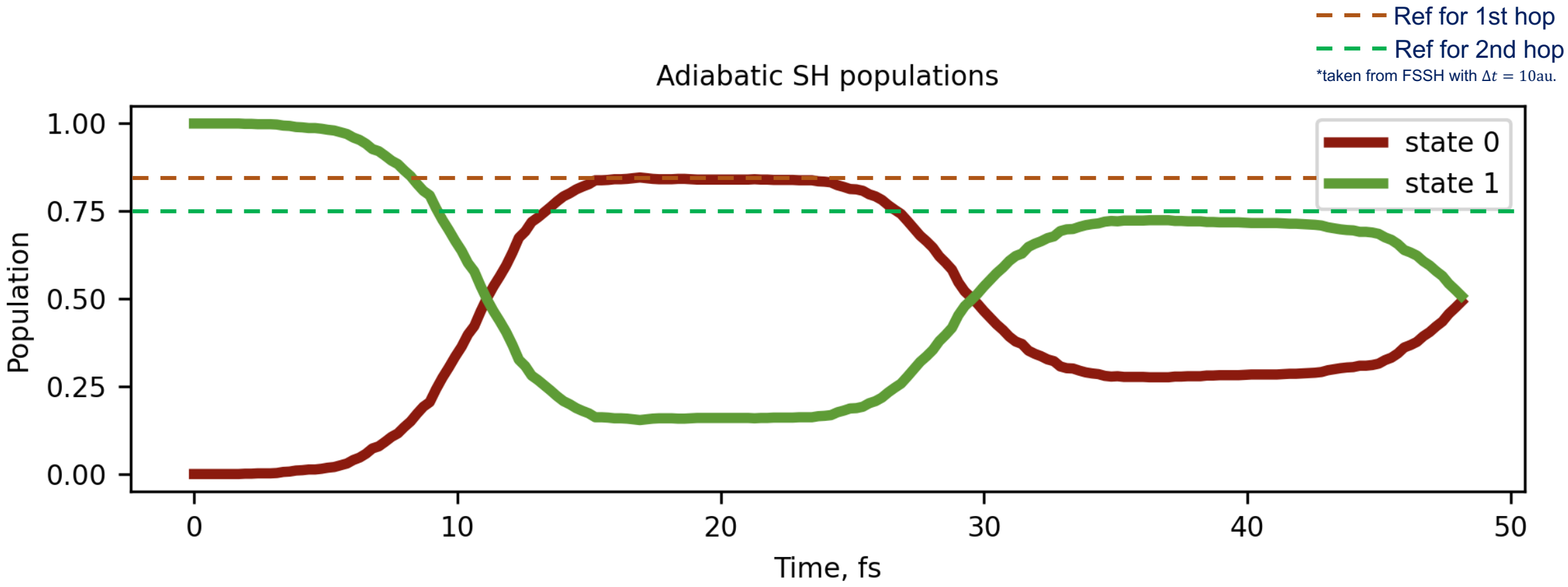
FSSH2 – $\Delta t = 50\text{au}$



FSSH2 – $\Delta t = 20\text{au}$

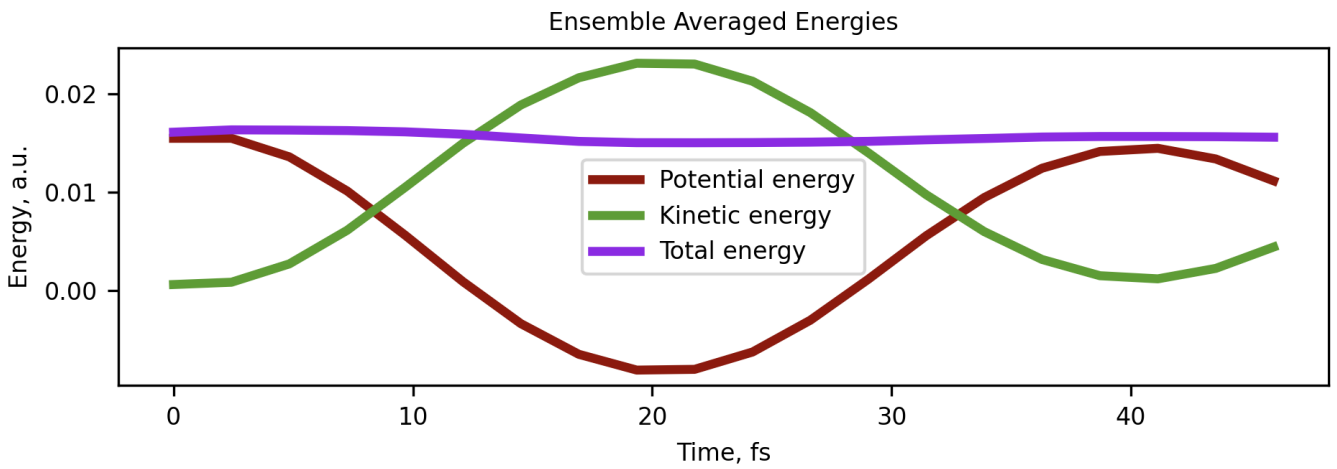


FSSH2 – $\Delta t = 10\text{au}$

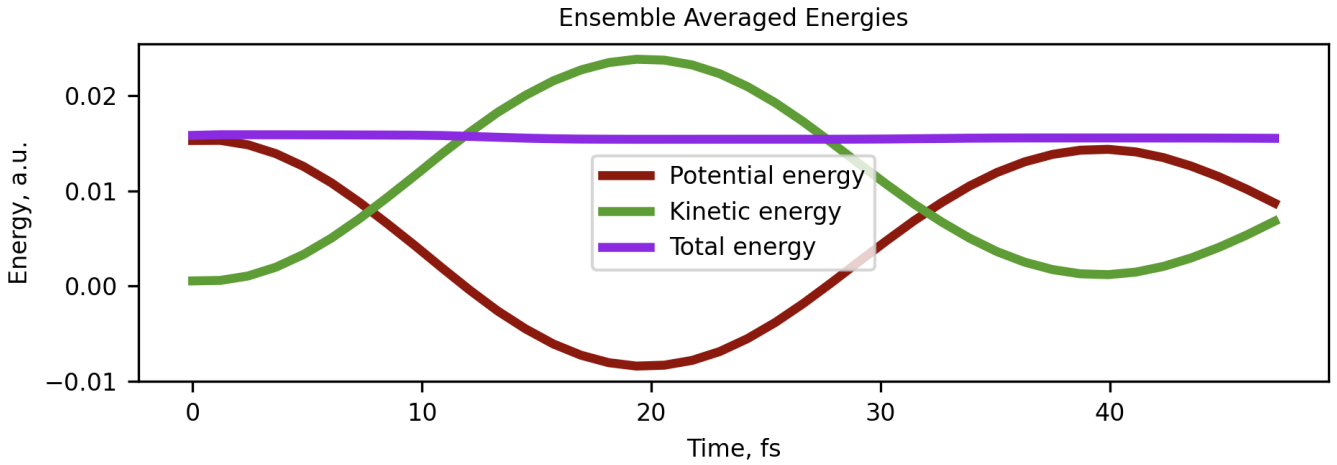


FSSH2 – energy conservation

$\Delta t = 100$:



$\Delta t = 50$:

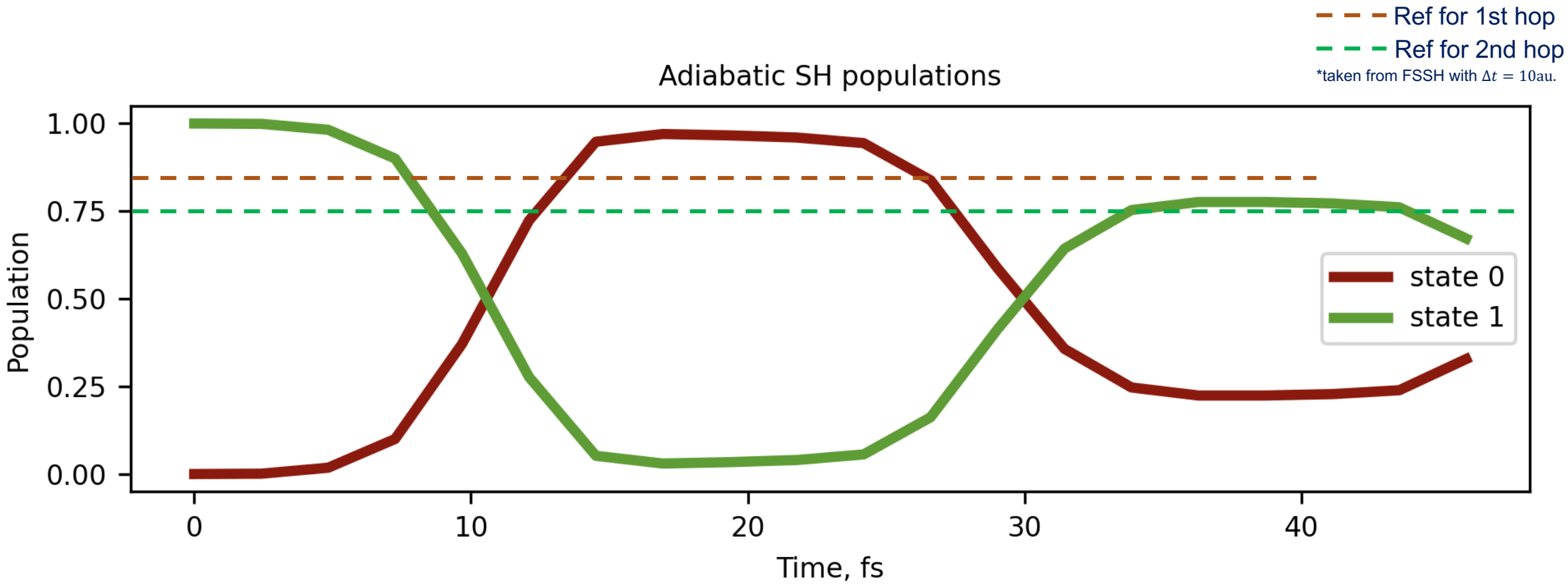


FSSH2 – observations

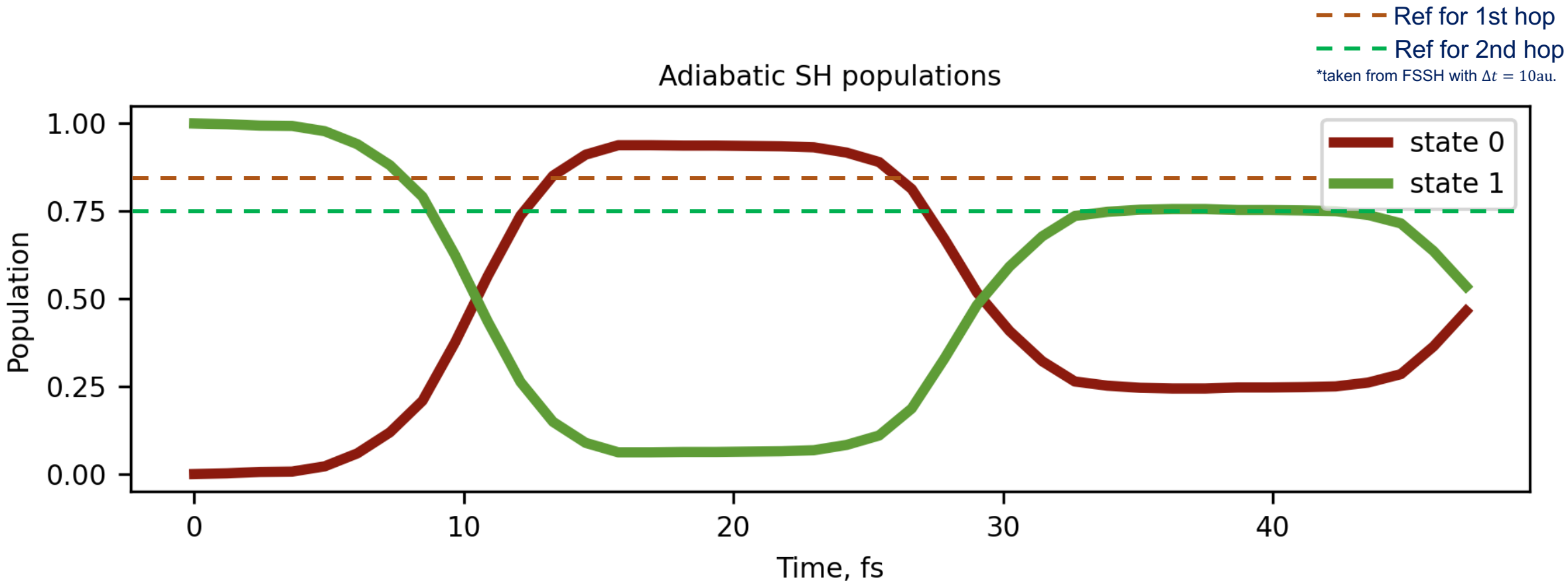
- Energy was already conserved at $\Delta t = 100\mathrm{au}$.

- Accordingly, FSSH2 provided converged results at around $\Delta t = 100\mathrm{au}$. (I could not try larger time step sizes since the system showed an error: division by zero)

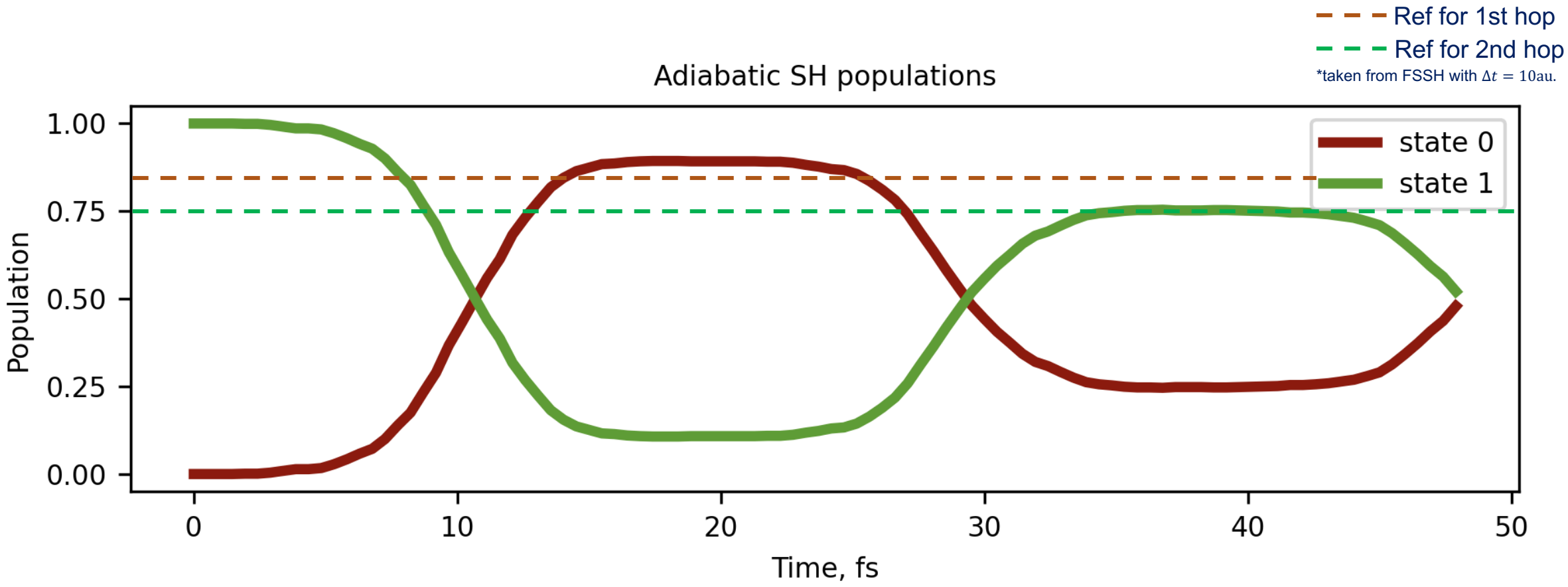
GFSH – $\Delta t = 100\text{au}$



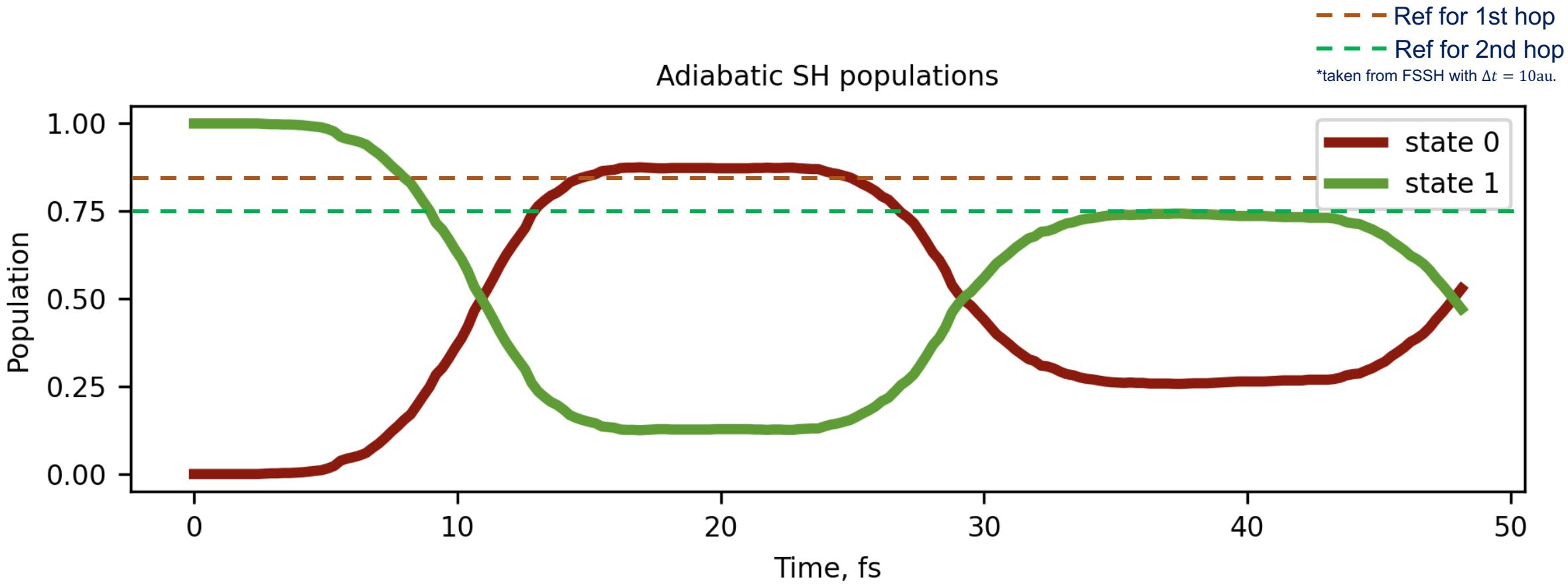
GFSH – $\Delta t = 50\text{au}$



GFSH – $\Delta t = 20\text{au}$

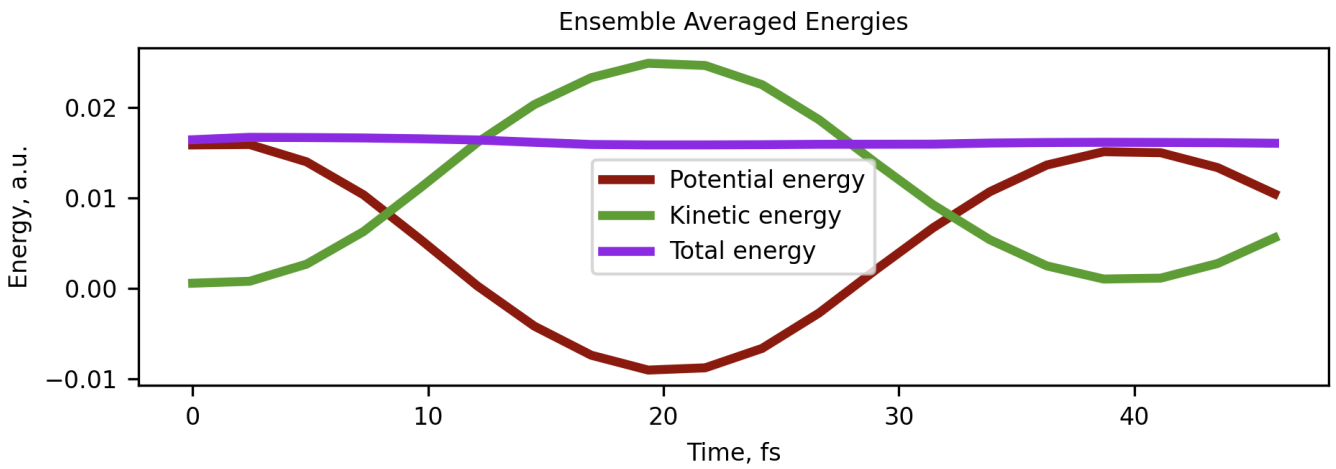


GFSH – $\Delta t = 10\text{au}$

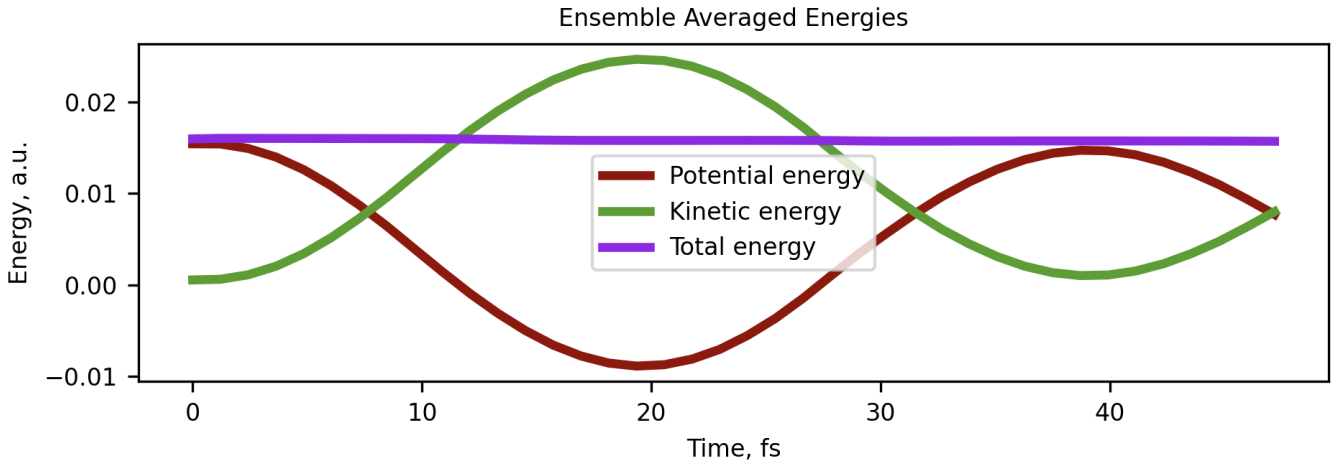


GFSH – energy conservation

$\Delta t = 100$:



$\Delta t = 50$:



GFSH – observations

- Same observations as for FSSH.

- It underperforms FSSH2, although their hop formulas are similar, because the implementation in Libra contains a Finite Element Method approximation of the original GFSH formula.

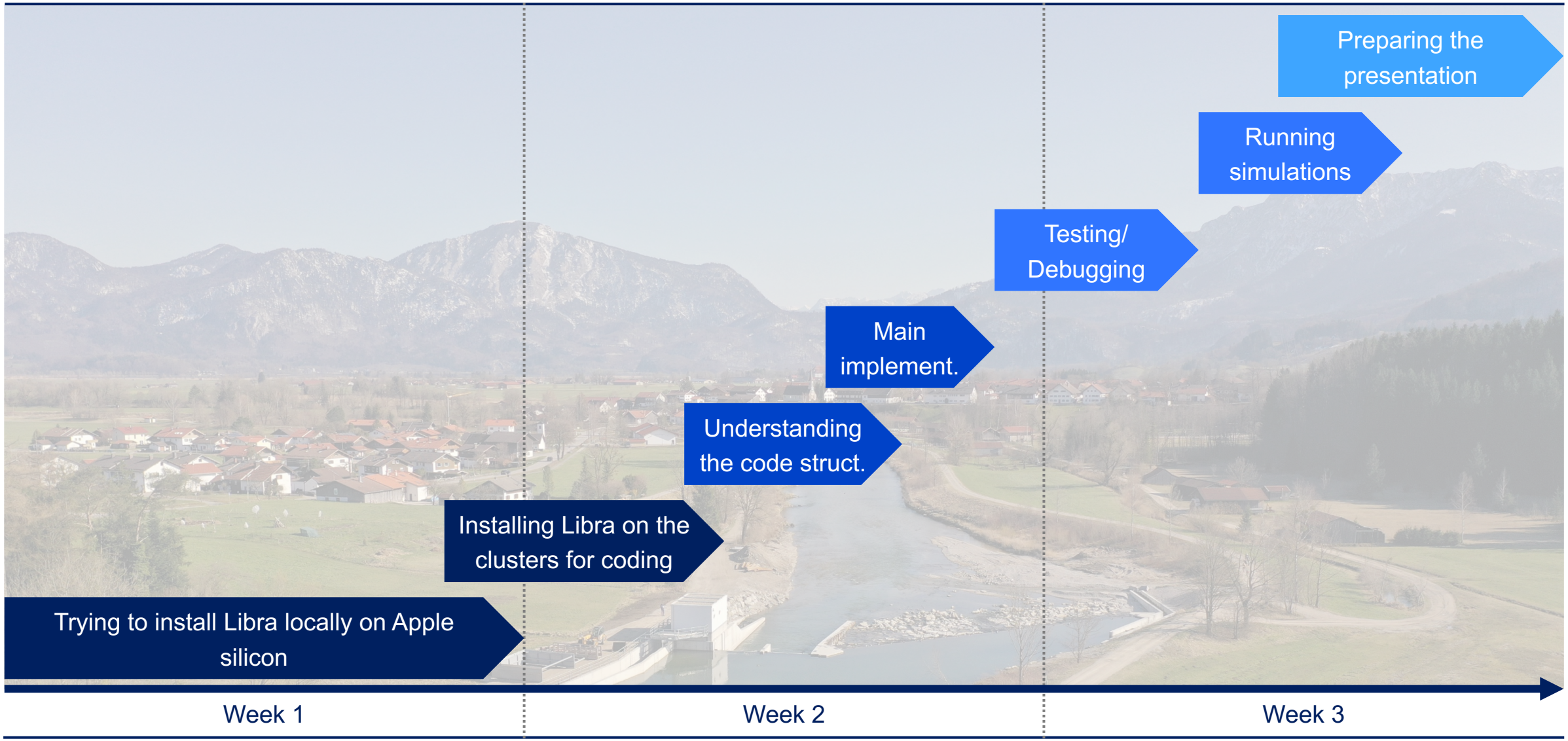
Conclusions

FSSH2 overperformed FSSH by significantly improving the populations for larger time steps and showing less sensitivity.

Energy conservation was no indicator of the convergence of FSSH2 but not of FSSH and GFSH.

Time & workflow overview

Time overview



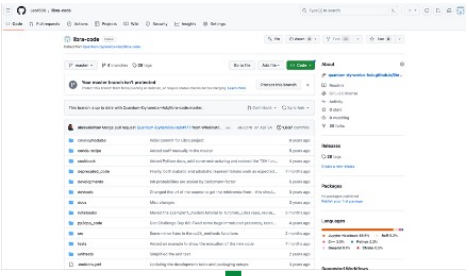
Workflow

CCR

Loc

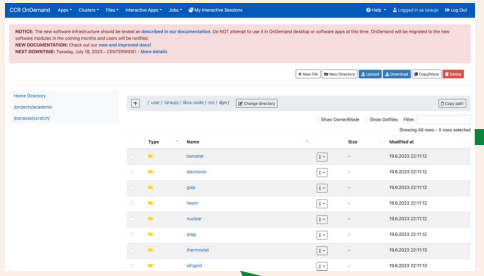
GitHub (Fork)

Pull from the Libra package



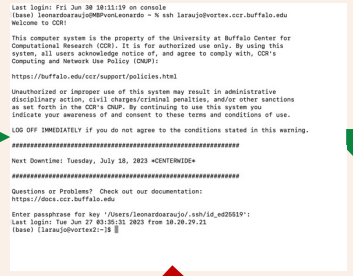
CCR OnDemand

Upload modifications



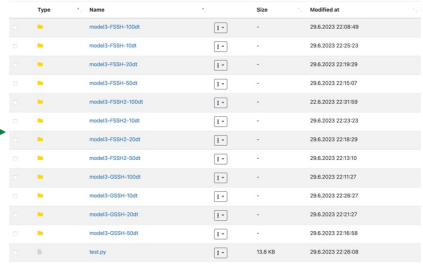
Terminal

Compile/test/simulate

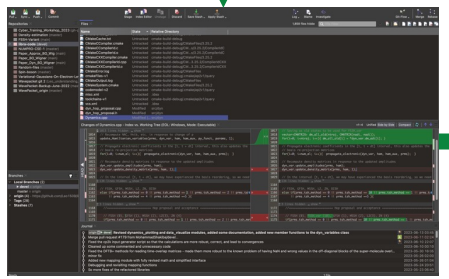


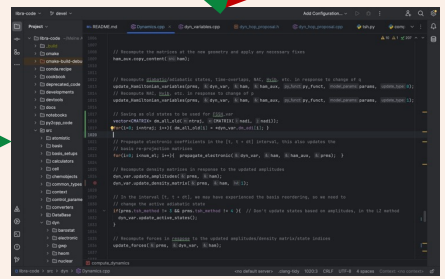
CCR OnDemand

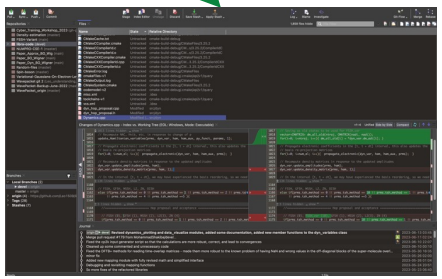
Download results



Implementation loop







SmartGit

Pull locally/observe modifications

CLion (C++ IDE)

Code/check syntax

SmartGit

Push modifications

Modified files: Dynamics.cpp

Saving densities of the previous time step:

```
// Recompute diabatic/adiabatic states, time-overlaps, NAC, Hvib, etc. in response to change of q
update_Hamiltonian_variables(prms, dyn_var, ham, ham_aux, py_funct, params, 0);
// Recompute NAC, Hvib, etc. in response to change of p
update_Hamiltonian_variables(prms, dyn_var, ham, ham_aux, py_funct, params, 1);

// Saving as old states to be used for FSSH_var
vector<CMATRIX> dm_all_old(ntraj, CMATRIX(nadi, nadi));
for(i=0; i<ntraj; i++){ dm_all_old[i] = *dyn_var.dm_adi[i]; }

// Propagate electronic coefficients in the [t, t + dt] interval, this also updates the
// basis re-projection matrices
for(i=0; i<num_el; i++){  propagate_electronic(dyn_var, ham, ham_aux, prms);  }
```

Setting tsh_method=10 as FSSH2:

```
// FSSH, GFSH, MSSH, LZ, ZN, DISH
else if(prms.tsh_method == 0 || prms.tsh_method == 10 || prms.tsh_method == 1 || prms.tsh_method == 2 |
     || prms.tsh_method == 4 || prms.tsh_method ==5 ){


  vector<int> old_states(dyn_var.act_states);

  //========================= Hop proposal and acceptance ==============================

  // FSSH (0), FSSH_var (10), GFSH (1), MSSH (2), LZ(3), ZN (4)
  if(prms.tsh_method == 0 || prms.tsh_method == 10 || prms.tsh_method == 1 || prms.tsh_method == 2 || p

    /// Compute hop proposal probabilities from the active state of each trajectory to all other states
    /// of that trajectory
    vector< vector<double> > g;
    g = hop_proposal_probabilities(prms, dyn_var, dm_all_old, ham, ham_aux);

    // Propose new discrete states for all trajectories
    vector<int> prop_states( propose_hops(g, dyn_var.act_states, rnd) );
```

Modified files: dyn_hop_proposal.h

Introducing a new method to compute hop probabilities with the previous densities as additional input:

```
vector< vector<double> > hop_proposal_probabilities(dyn_control_params& prms,
       dyn_variables& dyn_var, nHamiltonian& ham, nHamiltonian& ham_prev);

vector< vector<double> > hop_proposal_probabilities(dyn_control_params& prms,
       dyn_variables& dyn_var, vector<CMATRIX>& dm_all_old, nHamiltonian& ham, nHamiltonian& ham_prev);

//vector< vector<double> > hop_proposal_probabilities(dyn_control_params& prms,
//       dyn_variables& dyn_var, nHamiltonian& ham, vector<MATRIX>& prev_ham_dia);
```

Modified files: dyn_hop_proposal.cpp (1/2)

Introducing a new option in hop_proposal_probabilities(…) to compute FSSH2:

```
if(prms.tsh_method == 0){ // FSSH

g[traj] = hopping_probabilities_fssh(prms, dm, Hvib, dyn_var.act_states[traj]);

}
else if(prms.tsh_method == 10){ // FSSH_var

    //CMATRIX& dm_old = *dyn_var_old.dm_adi[traj];
    CMATRIX dm_old = dm_all_old[traj];

    g[traj] = hopping_probabilities_fssh_var(prms, dm, dm_old, Hvib, dyn_var.act_states[traj]);

}
else if(prms.tsh_method == 1){ // GFSH

g[traj] = hopping_probabilities_gfsh(prms, dm, Hvib, dyn_var.act_states[traj]);
```

Modified files: dyn_hop_proposal.cpp (2/2)

Compute FSSH2 in a new method hopping_probabilities_fssh_var(…):

```
        // Now calculate the hopping probabilities
        i = act_state_indx;

        sum = 0.0;
        double a_ii_old = denmat_old.get(i,i).real();
//  cout<<"a_ii = "<<a_ii<<endl;

        for(j=0;j<nstates;j++){

            if(i!=j){
            /**
                  dc/dt = -(i/hbar) * Hvib * c
                  (dc/dt)^+ = i/hbar * c^+ * Hvib^+

                  rho = c * c^+

                  P(i->j) = ( rho_jj - rho_old_jj ) / rho_ii

                */

                double a_jj_old = denmat_old.get(j,j).real();
                double a_jj     = denmat.get(j,j).real();

                if(a_ii_old<1e-8){ g_ij = 0.0; }  // avoid division by zero
                else{
                    g_ij = (a_jj - a_jj_old)/a_ii_old;  // This is a general case

                    if(g_ij<0.0){  g_ij = 0.0; }

                }// else

                g[j] = g_ij;
                sum = sum + g_ij;
            }
            else{ g[j] = 0.0; }

        }// for j

        g[i] = 1.0 - sum;

        return g;
```

Thank you for your attention!

Any questions?

Proooost!!
Karg