Mapping Approach to Surface Hopping (MASH)

CyberTraining Workshop
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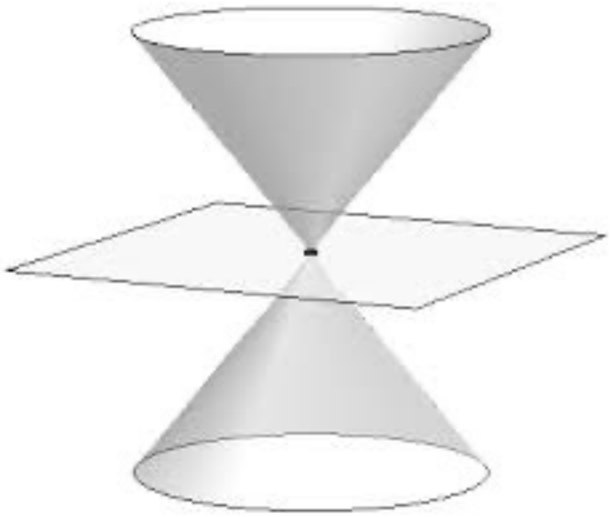

Non-adiabatic Dynamics

Electronic Component

$$\Psi(t, \mathbf{r}, \mathbf{R}) = \sum_i \chi_i(t, \mathbf{R}) \Phi_i(\mathbf{r}; \mathbf{R}(t))$$

Nuclear Component

Mapping Methods

- Ehrenfest, Meyer-Miller, spin mapping, CQM, SQC, …
- Often obtains mean field-like results through deterministic trajectories
- Excellent for capturing coherences
- Struggles with scattering, long-time populations

Surface Hopping Methods

- FSSH, GFSH, MSSH, BCSH, ID-A, SDM, DISH, …
- Stochastic hopping between electronic states
- Excellent for capturing populations
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Implementation Details

$$P_n = |c_n|^2 \qquad \alpha_N = \frac{N-1}{H_N - 1}$$

Initialization:

$$\phi_n = \frac{1}{N} + \alpha_N \left(P_n - \frac{1}{N} \right)$$

$$H_N = \sum_{n=1}^{N} \frac{1}{n}$$

- Population estimator transforms correctly with unitary operation
- Describes populations ($|n\rangle\langle n|$) and coherences ($|n\rangle\langle m|$) on equal footing

Hopping:

Run normal dynamics → Check if state with largest population changed

Check if state with largest population changed → Yes → Check if sufficient kinetic energy to accomplish hop

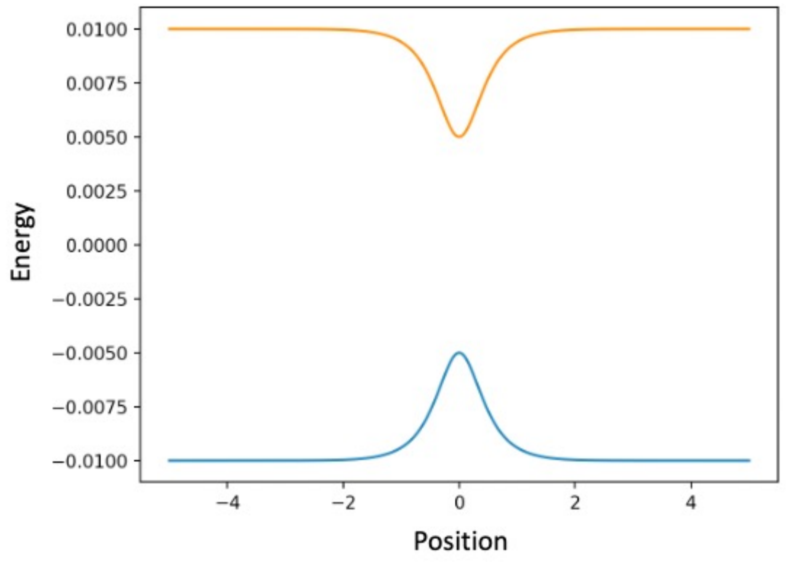
Check if state with largest population changed → No → Run normal dynamics

Check if sufficient kinetic energy to accomplish hop → Yes → Rescale momentum to conserve energy, change adiabatic state →

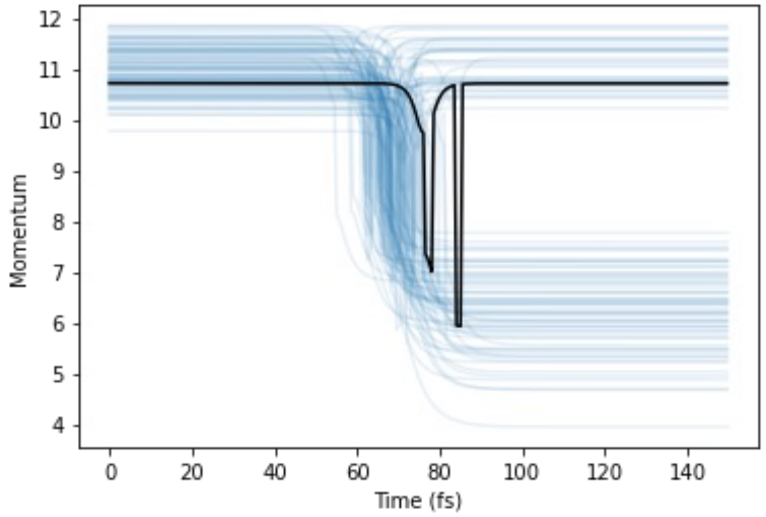
Check if sufficient kinetic energy to accomplish hop → No → Reverse momentum along non-adiabatic coupling vector, keep state →

Tully Model I

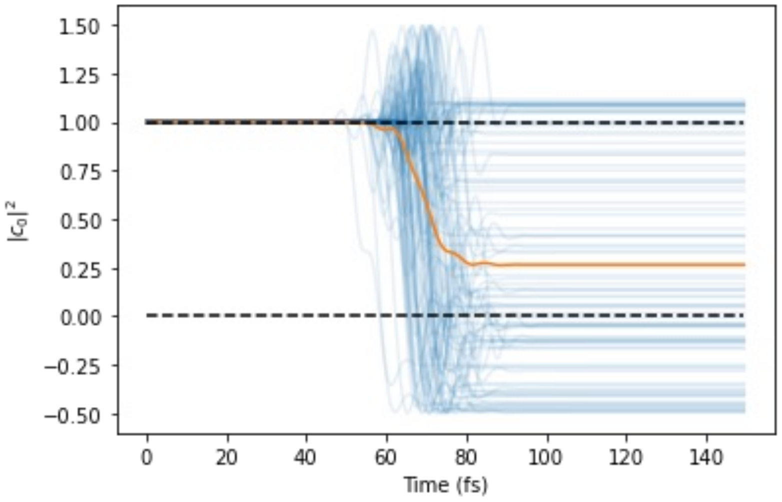
Adiabatic Potential



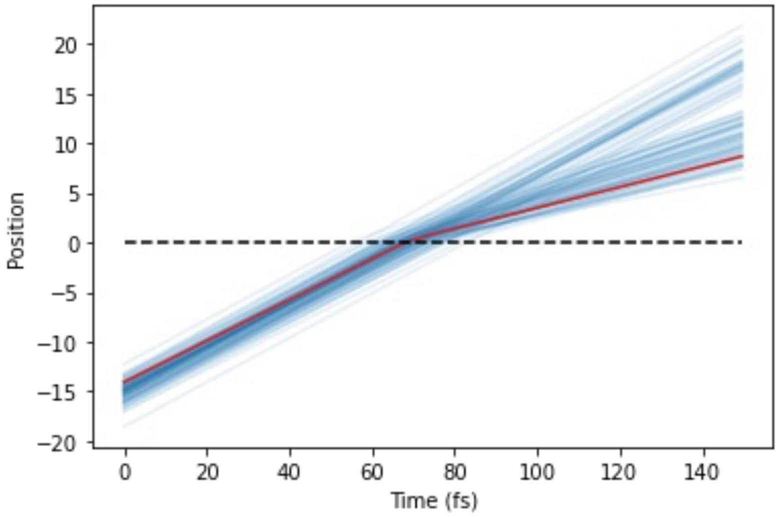
Trajectory Momenta



Ground State Population

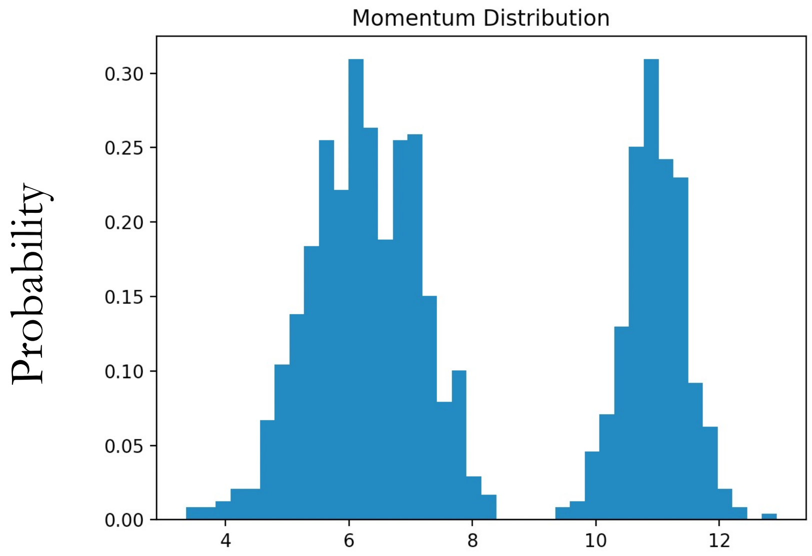


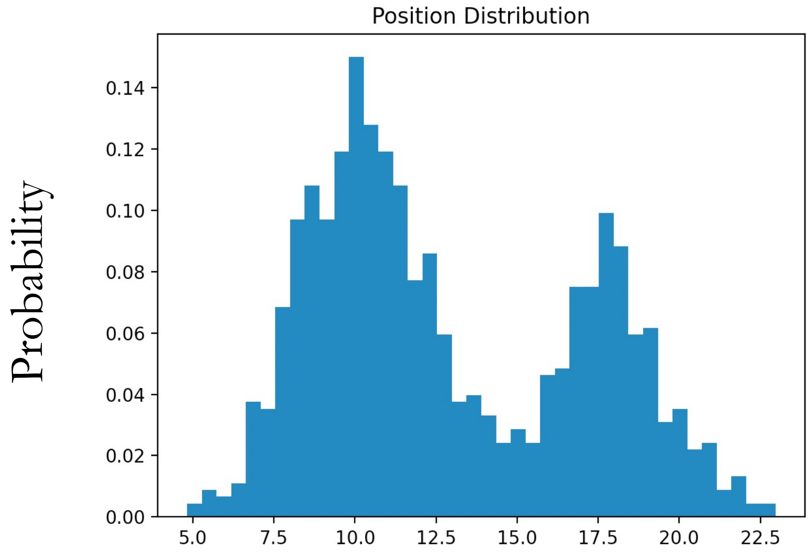
Trajectory Position



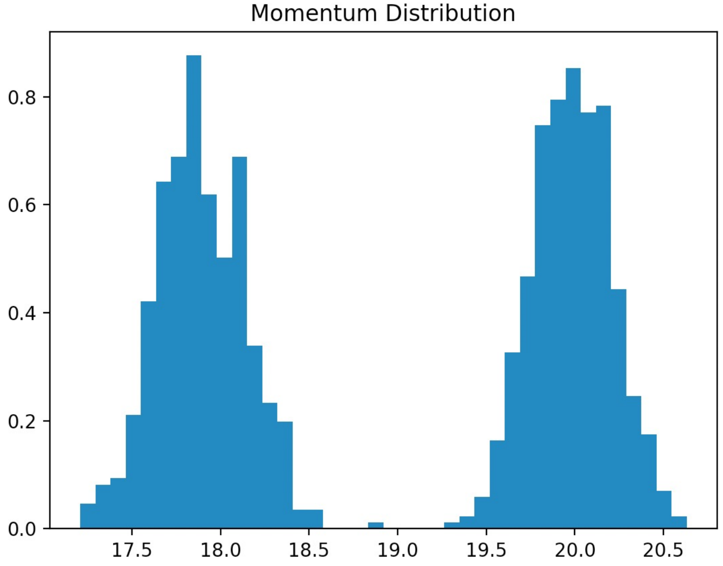
Tully Model I

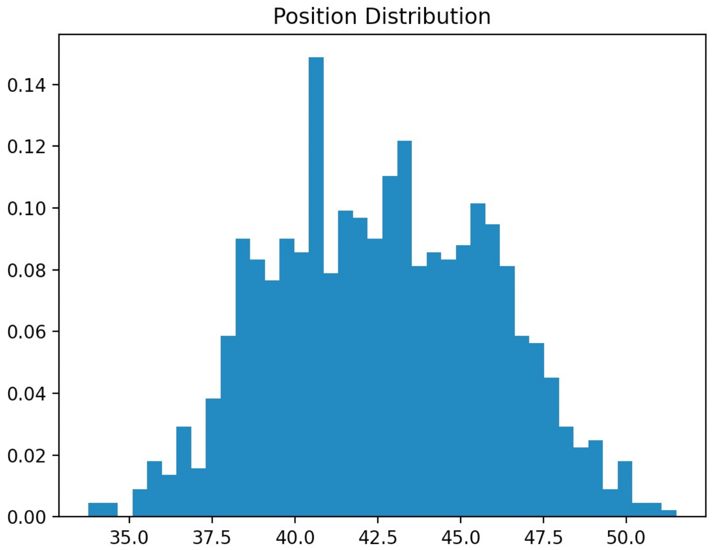
Low Energy





High Energy





- Could be converged further
- Successfully capture splitting like a surface hopping method
- Successfully capture coherences[1] (Fig. 5 of Runeson)