

CyberTraining Project: MASH

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I. INTRODUCTION

Accurately describing non-adiabatic dynamics continues to be a challenge especially in systems involving many levels and degrees of freedom. To address challenges of accurately yet efficiently calculating quantum dynamics, a variety of methods have been presented and are currently used. Here, I focus on two classes of methods. In the first, mapping methods like Ehrenfest dynamics evolve nuclear degrees of freedom on an average potential energy surface of all states in the system. In the right regimes, this can very accurately capture the coherences of classic models like the Fenna-Matthews-Olson (FMO) complex. These coherences are necessary for calculations of properties like multidimensional spectra. However, methods like Ehrenfest suffer from a failure to describe accurate populations and in particular, their long time limits. This lack of detailed balance is one reason an alternative class of methods is quite popular. Surface hopping methods largely solve the detailed balance issue and are excellent at describing the behavior of Tully models; however, this comes at the cost of correctly capturing coherences. Other challenges arise when attempting to extend any of these methods to larger, atomistic problems. Some methods in quantum dynamics, like MCTDH, require an analytic potential which forces a user to fit a model potential to electronic structure calculations before proceeding with dynamics. Other methods are best carried out in the diabatic picture require careful attention to a non-trivial diabaticization scheme before one can take standard adiabatic electronic structure calculations and apply them to the desired quantum dynamics.

II. MASH IMPLEMENTATION

A recently presented method was originally derived from a spin mapping picture and then extended to an arbitrary number of levels. This method is called the mapping approach to surface hopping (MASH) and it looks to merge the advantages of both surface hopping and mapping methods to capture both population and coherence behavior accurately.^{1,2} Here we describe the key features of this method including setting up initial conditions and how to implement the appropriate style of surface 'hop'.

A. Initial Conditions

Runeson and Manolopoulos derive a population estimator that correctly transforms under unitary operations. This estimator for each state, n , is

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

where N is total number of states, $P_n = |c_n|^2$, c_n are the coefficients for each electronic state,

$$\alpha_N = \frac{N-1}{H_N-1}, \quad (2)$$

and $H_N = \sum_{n=1}^N 1/n$. Ultimately, regardless of basis chosen, the estimated average populations, $\langle \Phi_n \rangle$, correctly recapture the proper equilibrium statistics. In turn, the condition on initial conditions when trying to describe a state $|n\rangle\langle n|$ becomes

$$P_m = \frac{\delta_{nm}}{\alpha_N} + \frac{\alpha_N - 1}{N\alpha_N}. \quad (3)$$

This only constrains the magnitude of the coefficients, the phase is chosen randomly from a uniform distribution. It is also worth noting that correct transformation under unitary operations means that coherences can be calculated on the same footing as populations. There is just a simple rotation between them and they are no harder to describe correctly than the populations.

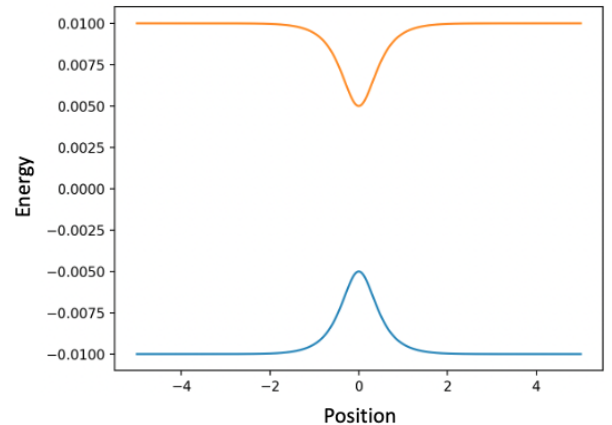


Figure 1. Tully Model of the first kind in the adiabatic basis. Simulations are initialized to the left of the avoided crossing moving rightward on the ground state (blue) and can hop up to the excited state (yellow) in the region of strong coupling near $q = 0$.

B. Hopping Procedure

With the electronic initial conditions specified and nuclear initial conditions dependent on the particular problem of interest, the next step is to evolve this state in time. A simple

velocity-Verlet scheme is sufficient in which the nuclear degrees of freedom evolve on the adiabatic state with the largest instantaneous population. After each time step, if the identity of the largest population changes, a hop is proposed to the potential energy surface of the new state. Hops are accepted or rejected based on whether the total kinetic energy of the nuclei is sufficient to overcome the change in potential energy. When a hop is accepted, the momentum is scaled along the non-adiabatic coupling vector to conserve energy. When the hop is rejected (a frustrated hop) the momentum is reversed along the same non-adiabatic coupling vector. One of the most notable features of the MASH procedure is that the dynamics are deterministic. As a result, it's possible to improve the accuracy of the dynamics by utilizing an adaptive time step. When a hop happens during a particular step, the dynamics evolve for that full step on the original surface rather than switching exactly at the appropriate instant. In addition, when several states are close to each other in population, a single step has the possibility of making a double jump and skip past important physical interactions. Whenever a hop is proposed, the step can be iteratively split and run twice with half the time step until energy is conserved up to an acceptable threshold.

C. The Code Itself

Most of the MASH algorithm is implemented in Libra and the updated files are included in my project repository on GitHub. However, after implementing the initialization function for MASH, I struggled to chase down a segmentation fault that brought my work to a temporary halt. I hope to work more closely with Alexey or one of his students soon to parse through the interactions and make this method more easily available. In the mean time, I also implemented a simple, independent version in Python which is also available on GitHub.

III. RESULTS

As an initial test for this iteration of the code and demonstration of properties MASH can accurately capture, I first consider a variation of Tully's model of the first kind. The potential in the diabatic basis is

$$\hat{V}(q) = \kappa(q)\hat{\sigma}_z + \Delta(q)\hat{\sigma}_x \quad (4)$$

where

$$\kappa(q) = A \tanh(Bq), \quad (5)$$

$$\Delta(q) = C e^{-Dq^2}, \quad (6)$$

$A = 0.01$, $B = 1.6$, $C = 0.005$, and $D = 1$ (Figure 1). The electronic system is initialized in the ground state and nuclear degrees of freedom are initialized according to Gaussian

distributions centered at \bar{q} and \bar{p} with inversely proportional standard deviations described by $2\sigma^2 = \gamma$ and $2\sigma^2 = 1/\gamma$. The results shown (Figure 2) could be converged a little further; however, already the overall behavior is becoming clear. Like standard surface hopping methods, this approach correctly and cleanly splits the momentum distributions between components that stay on the ground state moving quick and those that transition to the excited state and are moving more slowly. As with exact calculations (see slides for more figures highlighting these results) the position distributions are not entirely separated. However, my implementation clearly still has what will hopefully be a minor error because MASH and surface hopping methods should be getting relative peak intensities correct as well but we are not here. In the low energy regime, the slower (left peak) of both position and momentum corresponds to excitation and should be less probable than remaining on the ground state. Peak positions are in good agreement with previous work but their relative intensities are suggesting this existence of an error.

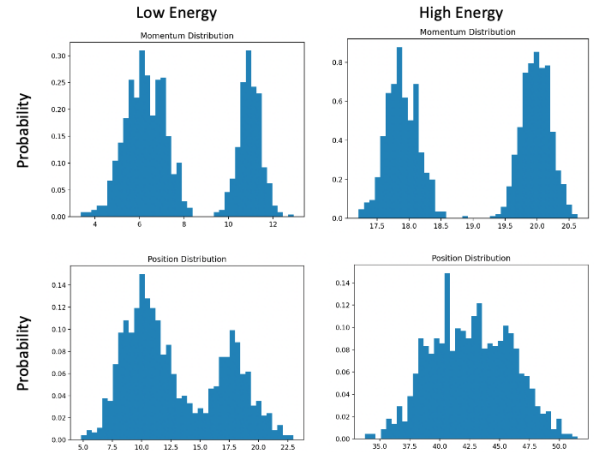


Figure 2. Position and momentum probability distributions from an ensemble of trajectories initialized with low energy ($\bar{q} = -15, \bar{p} = 10.95, \gamma = 0.5$) and high energy ($\bar{q} = -15, \bar{p} = 20, \gamma = 0.1$).

IV. CONCLUSION

While the case calculated here is just for a 2-level system, the procedure is flexible enough to be applied to any number of electronic states and nuclear degrees of freedom. The next step is to find and correct the errors in these codes and then begin applying the method to calculate spectra and other properties for model systems and eventually fully atomistic ones as well.

REFERENCES

- ¹J. R. Mannouch and J. O. Richardson, *The Journal of Chemical Physics* **158**, 104111 (2023).
- ²J. E. Runeson and D. E. Manolopoulos, arXiv:2305.08835.