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## Communication: The correct interpretation of surface hopping trajectories: How to calculate electronic properties

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In a recent paper, we presented a road map for how Tully's fewest switches surface hopping (FSSH) algorithm can be derived, under certain circumstances, from the mixed quantum-classical Liouville equation. In this communication, we now demonstrate how this new interpretation of surface hopping can yield significantly enhanced results for electronic properties in nonadiabatic calculations. Specifically, we calculate diabatic populations for the spin-boson problem using FSSH trajectories. We show that, for some Hamiltonians, without changing the FSSH algorithm at all but rather simply reinterpreting the ensemble of surface hopping trajectories, we recover excellent results and remove any and all ambiguity about the initial condition problem. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4837795>]

### I. INTRODUCTION

Tully's fewest switches surface hopping (FSSH) algorithm has been among the most popular approaches for nonadiabatic electron transfer.<sup>1–4</sup> FSSH owes this widespread popularity to its extreme simplicity and computational efficiency. However, these benefits come with a cost. There are several unresolved questions that result from surface hopping's origin as an intuitively derived and empirically justified algorithm. These questions include: (1) Given that trajectories move along adiabatic surfaces according to the FSSH algorithm, how can diabatic electronic populations be estimated? (2) More generally, how can we calculate the expectation value of any electronic operator from a swarm of trajectories given that there is no full vibronic surface-hopping wavefunction? (3) What are the correct initial conditions to impose on FSSH calculations when the electronic state at time zero is not an adiabatic wavefunction?

In this communication we address these questions from a new perspective using our recently discovered connection between FSSH and Kapral and Martens' mixed quantum-classical Liouville equation (QCLE).<sup>5–10</sup> This FSSH-QCLE connection provides an unambiguous definition of the FSSH mixed quantum-classical nuclear-electronic density matrix, and the latter can be used to calculate any desired electronic property. In the end, our results will highlight that for some Hamiltonians, *even without decoherence*,<sup>11</sup> standard FSSH trajectories can estimate a host of electronic properties quite well provided one uses the correct interpretation of the FSSH algorithm.

### II. THEORY: BASIS SET CONVERSION

Historically, determining electronic properties from a swarm of FSSH trajectories has not been simple.<sup>12–15</sup> As mentioned above, FSSH's problems stem from the lack of a full vibronic wavefunction or density matrix for calculating observable quantities. Moreover, in practice, the calculation of

electronic properties from FSSH trajectories is complicated because each trajectory carries both an active electronic surface (henceforward,  $\lambda$ ) and an electronic wavefunction, effectively double counting the electronic state. If we are interested in populations on adiabatic surfaces, then a great deal of research has concluded that we should count only the active surface information and disregard the electronic wavefunctions on each trajectory.<sup>1</sup> After all, FSSH trajectories move along adiabatic surfaces and the active surface data obey detailed balance approximately, whereas the electronic wavefunctions can become meaningless at long times.<sup>16,17</sup> That, being said, one common problem in the quantum dynamics community is the calculation of diabatic populations. In this paper, we will explore this problem and present the definitive solution.

As might be expected from our discussion above, two common and unsatisfying methods exist in the literature for estimating diabatic populations from a swarm of FSSH trajectories.<sup>13,14,18</sup> One method uses exclusively the electronic wavefunction of each trajectory. The other uses only the active surface of each trajectory. Each method has its benefits and faults. We review these methods now. Afterward, we give a third approach that arises as the direct result of the analytical theory in Ref. 19. The practical reader will notice that this third method coincidentally interpolates between the previous two approaches and captures the best of both worlds.

**Notation.** In this article,  $i, j$  will represent adiabatic electronic surfaces, and  $a$  will represent a diabatic electronic state. We always run FSSH trajectories along adiabatic surfaces with electronic wavefunctions defined by

$$|\psi_{el}\rangle = \sum_i c_i |\Phi_i\rangle. \quad (1)$$

For a diabatic basis  $\{|\Xi_a\rangle\}$  defined by  $|\Phi_i\rangle = \sum_a U_{ai} |\Xi_a\rangle$ , the FSSH electronic wavefunction can be written as

$$|\psi_{el}\rangle = \sum_a \left( \sum_i U_{ai} c_i \right) |\Xi_a\rangle \equiv \sum_a b_a |\Xi_a\rangle, \quad (2)$$

where  $U$  depends on the position  $R$  of the surface hopping trajectory.

### A. Method 1: Surfaces

The most straightforward method of converting between bases uses the active surface. From this framework, a trajectory moving along a given active surface can be considered to move along one or more diabats according to the diabatic-adiabatic transformation. In other words, one ignores the electronic wavefunction completely. Mathematically, for a trajectory moving along active adiabatic surface  $\lambda$ , the probability of measurement on diabat  $a$  is  $|U_{a\lambda}(R)|^2$  and the average population on  $a$  for a swarm of trajectories is

$$P_a = \frac{1}{N} \sum_l^N |U_{a\lambda^l}(R^l)|^2. \quad (3)$$

Here, the sum is over  $N$  trajectories (labeled by  $l$ ) with nuclear position and momentum  $R^l$  and  $P^l$  and active surface  $\lambda^l$ .

### B. Method 2: Electronic wavevector

An alternate method to calculate diabatic populations is to use exclusively the electronic wavefunctions of each surface hopping trajectory. Once this choice is made the conversion between bases follows Eq. (2). The probability for one FSSH trajectory to be measured in diabatic state  $a$  is therefore  $|b_a|^2 = |\sum_i U_{ai}(R)c_i|^2$  and the average population on  $a$  for a swarm of  $N$  trajectories is

$$P_a = \frac{1}{N} \sum_l^N \left| \sum_i U_{ai}(R^l)c_i^l \right|^2. \quad (4)$$

Note that the active surface  $\lambda^l$  does not enter this formulation.

### C. Method 3: Mixed quantum-classical density

According to Ref. 19, a rigorous theory of FSSH trajectories can be made by constructing the corresponding nuclear-electronic density matrix  $\mathbf{A}(R, P)$ .  $\mathbf{A}(R, P)$  can then be compared rigorously to the partial Wigner transform (transforming over only nuclear coordinates) of the exact (nuclear plus electronic) wavefunction. Intuitively,  $A_{ii}(R, P)$  should be the population on adiabat  $i$  at position  $(R, P)$  in phase space, and  $A_{ij}(R, P)$  should be the transition amplitude between the nuclear wavefunction on adiabat  $i$  and the nuclear wavefunction on adiabat  $j$  at  $(R, P)$  in phase space.

With this in mind, according to Ref. 19, the correct off-diagonal density matrix element for a swarm of FSSH trajectories is defined by the active surface  $\lambda$ :

$$A_{ii}(R, P) = \frac{1}{N} \sum_l^N \delta(R - R^l(t))\delta(P - P^l(t))\delta_{i,\lambda^l(t)}. \quad (5)$$

The off-diagonal components are less straightforward than the diagonal components, but take the following forms:<sup>19</sup>

$$A_{ij}^{(i)}(R, P) = \frac{1}{N} \sum_l^N \delta(R - R^l(t))\delta(P - P^l(t))\delta_{i,\lambda^l(t)} \frac{\sigma_{ij}^l}{\sigma_{ii}^l}, \quad (6)$$

$$A_{ij}^{(j)}(R, P) = \frac{1}{N} \sum_l^N \delta(R - R^l(t))\delta(P - P^l(t))\delta_{j,\lambda^l(t)} \frac{\sigma_{ij}^l}{\sigma_{jj}^l}. \quad (7)$$

Here  $\sigma_{ij}$  is the electronic density matrix ( $\sigma_{ij} = c_i c_j^*$ ).

As discussed in Ref. 19, the definitions in Eqs. (6) and (7) should and would be equal for an improved FSSH algorithm that incorporated decoherence. For standard Tully FSSH, however, these two different definitions of the off-diagonal density matrix element may be unequal, and so one can even consider an average of the two. Thus, besides Eqs. (6) and (7), in this paper, we will also consider  $\frac{1}{2}(A_{ij}^{(i)} + A_{ij}^{(j)})$  and

$$A_{ij}(R, P) = \frac{1}{N} \sum_l^N \delta(R - R^l(t))\delta(P - P^l(t))\sigma_{ij}^l \quad (8)$$

as two other possible definitions of the off-diagonal matrix element. Equation (8) can be considered the average of Eqs. (6) and (7) with weights proportional to the active populations on each adiabat.

Armed with  $A_{ij}$ , we can now convert basis easily. For a density matrix  $A$  in the adiabatic basis, the density matrix  $B$  in the diabatic basis is

$$B(R, P) = U(R)A(R, P)U^\dagger(R), \quad (9)$$

and the population on diabat  $a$  at  $(R, P)$  is

$$B_{aa} = \sum_i A_{ii}|U_{ai}|^2 + \sum_{i<j} 2\text{Re}(U_{ai}A_{ij}U_{aj}^*). \quad (10)$$

Finally, the total population on diabatic surface  $a$  is then the trace over nuclei. For example, using Eq. (8):

$$P_a = \int dR dP B_{aa}(R, P) = \frac{1}{N} \left( \sum_l^N \sum_i |U_{ai}|^2 \delta_{i,\lambda^l} + \sum_l^N \sum_{i<j} 2\text{Re}(U_{ai}\sigma_{ij}^l U_{aj}^*) \right). \quad (11)$$

Intuitively, it is now clear that a swarm of FSSH trajectories on each surface represents a sampling of a classical density; the resulting trace can then be understood as a Monte Carlo integral evaluation with the FSSH particle density serving as the weighting function.

The reader should note that the diabatic populations in Eq. (11) are not guaranteed to be positive. However, one should find physically meaningful (positive) populations when, statistically, the electronic surface populations are consistent with the electronic wavefunctions of each trajectory.

## III. RESULTS

### A. Spin-boson Hamiltonian

To prove the validity of Eq. (11) above, we now study the spin-boson Hamiltonian. We will plot the population on one diabat as a function of time. If we isolate the mode ( $x$ ) coupled

to the individual two-level system, the spin-boson Hamiltonian is

$$H = \frac{p^2}{2M} + \frac{1}{2}M\Omega^2x^2 + \left(\lambda x + \frac{\epsilon_0}{2}\right)\sigma_z + V\sigma_x + \sum_{\alpha} \left( \frac{\pi_{\alpha}^2}{2m_{\alpha}} + \frac{1}{2}m_{\alpha}\omega_{\alpha}^2 \left( z_{\alpha} - \frac{\zeta_{\alpha}}{m_{\alpha}\omega_{\alpha}^2}x \right)^2 \right), \quad (12)$$

where  $M$  is the mass,  $\Omega$  is the natural frequency,  $V$  is the diabatic coupling,  $\epsilon_0$  is the driving force, and  $\lambda$  is related to the reorganization energy  $E_r$  by  $\lambda = \sqrt{E_r M \Omega^2 / 2}$ . For our surface hopping calculation, we take the  $x$  coordinate as our nuclear coordinate, and we take the Pauli matrices to be in the basis of diabatic electronic states. Using these identifications, the harmonic bath can be integrated out, and for an Ohmic spectral density, one finds a simple classical Langevin force in one dimension with damping parameter  $\gamma$ . Mathematically, if  $g(\omega)$  is the density of states for the harmonic bath,  $\gamma \equiv \pi g(\omega_{\alpha})\zeta_{\alpha}^2 / (2Mm_{\alpha}\omega_{\alpha}^2)$  is a constant.

We compare our surface-hopping results (one dimensional with friction) versus Ehrenfest (one dimensional with friction) versus numerically exact QUAPI results.<sup>20–22</sup> For the QUAPI (quasi-adiabatic propagator path integral) method our Hamiltonian corresponds to a spin interacting with an environment through a Brownian oscillator spectral density:<sup>13,23,24</sup>

$$J(\omega) = \frac{1}{2} \frac{E_r \Omega^2 \gamma \omega}{(\omega^2 - \Omega^2)^2 + \gamma^2 \omega^2}. \quad (13)$$

To test the validity of Eq. (11), we will look at two different regions of parameter space: Case A is in between the Redfield and nonadiabatic Marcus regime (Fig. 1); Case B is in the nonadiabatic Marcus regime (Fig. 2).

## B. Initial conditions

As another test of the approach in Ref. 19, in this communication we choose our reorganization energy and driving force so that the system is in the barrierless regime ( $\epsilon_0 = E_r$ ). As such, our initial conditions are clearly not restricted to a single adiabat. Instead, we must convert our initial electronic wavefunction from a diabatic basis to an adiabatic basis. We must also recognize that, correspondingly, some FSSH trajectories will start off on active adiabatic surface 1, while others will start on active adiabatic surface 2. Finally, for the surface hopping data, we choose entirely classical (Boltzmann) initial conditions for positions and momenta; the QUAPI data are sampled from quantum mechanical initial conditions.

## C. Case A

For our first model problem we consider the parameter regime  $V = E_r$ . In this regime, decoherence is not paramount and FSSH should give reasonable results. In fact, A-FSSH and FSSH results are identical. As shown in Fig. 1(a), methods #1 and #2 give nonsensical results, while method #3 works rather well over all time. As would be expected from Refs. 16 and 17, the surface method (method #1) works at long times, recovering detailed balance approximately (as compared with

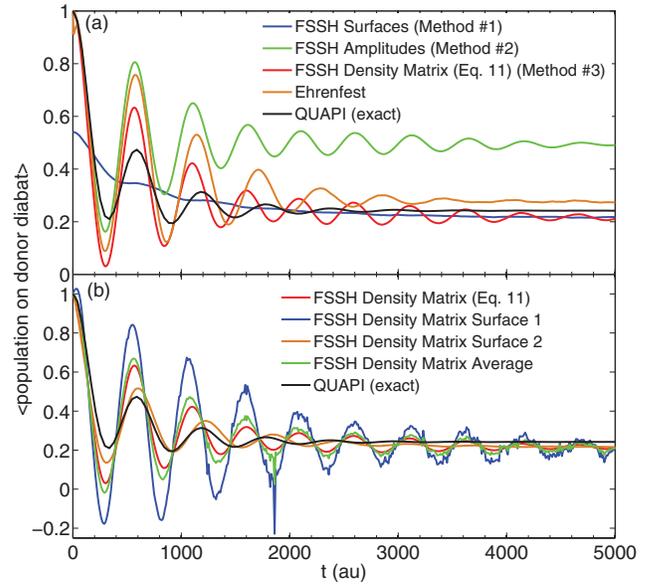


FIG. 1. (a) Diabatic population as a function of time using the different basis conversion methods. We compare with the exact QUAPI population and the Ehrenfest population. (b) Diabatic populations comparing different possible realizations of method #3. Parameters are:  $M = 1$ ,  $\Omega = 0.021375$ ,  $V = 0.00475$ ,  $E_r = 0.00475$ ,  $\epsilon_0 = 0.00475$ ,  $\gamma = 0.04275$ ,  $kT = 0.00095$ . Surface hopping and Ehrenfest: 10 000 trajectories with timestep = 0.01. QUAPI: timestep = 0.2 and  $\Delta k_{max} = 9$ .

the exact QUAPI populations). However, the method is nonsensical at time  $t = 0$  because transforming between adiabatic and diabatic representations according to surface is not reversible. Thus, the method does not even recover the correct initial conditions.

Method #2 suffers the opposite problem. Admittedly, the method incorporates off-diagonal density matrix elements

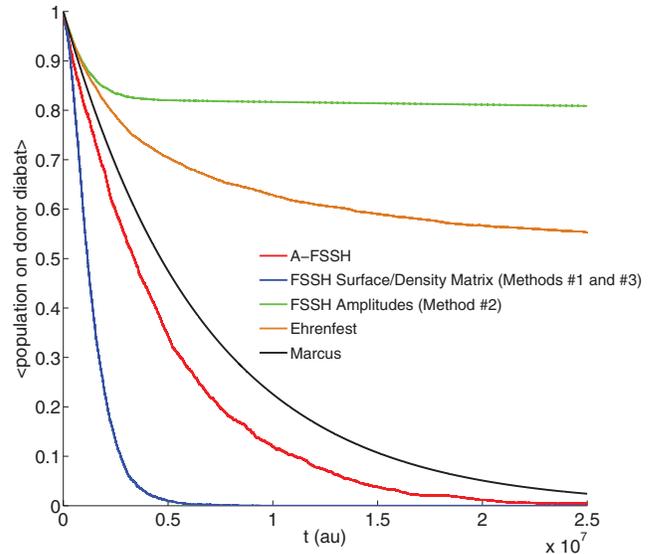


FIG. 2. Diabatic population as a function of time using the different basis conversion methods. We compare with the Marcus and Ehrenfest populations. (Note: All three methods produce the same results for A-FSSH and methods #1 and #3 agree for FSSH.) Parameters are:  $M = 1$ ,  $\Omega = 0.00004375$ ,  $V = 0.00002$ ,  $E_r = 0.0239$ ,  $\epsilon_0 = 0.0239$ ,  $\gamma = 0.00015$ ,  $kT = 0.00095$ . 2000 trajectories with timestep = 1.25.

(and thus is reversible); at short times, the method recovers the correct oscillatory behavior. However, at long times the wavefunctions become meaningless and do not recover the correct asymptotic populations (to match detailed balance). This agrees with Refs. 16 and 17 as well.

The density matrix method (i.e., method #3) combines the best of methods #1 and #2, giving nearly the correct population over the entire time range. It also outperforms Ehrenfest in this regime. The small oscillations at long time are likely due to a lack of decoherence in the FSSH algorithm.

With regards to choice of off-diagonal element, Fig. 1(b) shows the effects of different choices for  $A_{12}$  (Eqs. (6)–(8)). From our experience, we believe the method using Eq. (8) is optimal. Equation (8) should be the most stable since it does not require a density component in the denominator. Interestingly, the numerical results with  $A_{12}$  from surface 2 show the best performance here; for the moment, we are unsure why this is so. Future research might well explore this happenstance: is it meaningful or coincidental?

#### D. Case B

For our second model problem, we provide numerical data from the nonadiabatic Marcus regime ( $V \ll E_r$ ), which we have studied recently.<sup>25</sup> According to Fig. 2, methods #2 and #3 perform at roughly the same level of accuracy. In this regime, the coupling region is narrow and a single adiabat corresponds to a single diabats almost everywhere in position space—hence basis conversion by surface is almost reversible. However, the wavefunction method still cannot recover detailed balance at long times. The Marcus regime also proves to be a stronger test for Ehrenfest, and the latter does not recover detailed balance.<sup>13,16,17</sup>

Figure 2 reiterates a point we have made previously:<sup>25</sup> the decoherence problem is significant for FSSH in the nonadiabatic Marcus regime, where FSSH always overestimates the transition rate between diabats. To illustrate this fact, we include data using our augmented A-FSSH dynamical scheme to incorporate decoherence. Note that while the FSSH amplitudes do not properly obey detailed balance, the A-FSSH amplitudes do. The reasoning is simple: decoherence events in A-FSSH project the wavefunction onto the active surface of the trajectory and thus restore the internal consistency of the surface-hopping algorithm. Since the surface data roughly satisfy detailed balance at long times, adding decoherence makes the wavefunction obey detailed balance as well.

Finally, the reader will note that all three methods (#1, #2, #3) in Fig. 2 numerically give the same diabatic populations for A-FSSH. In general, for a Hamiltonian outside the nonadiabatic Marcus regime, we believe that methods #2 and #3 would both outperform method #1, if an exact treatment of decoherence were possible. However, given that all schemes to incorporate decoherence on top of surface-hopping are necessarily approximate, method #3 is clearly the optimal method

by which one should calculate diabatic electronic properties in general.

#### IV. CONCLUSION

In this communication we have shown the correct way to convert between electronic bases within the context of the FSSH algorithm. Our method was chosen from our knowledge of the correct mixed quantum-classical density matrix that corresponds to a swarm of surface hopping trajectories, as presented in Ref. 19. The results above are strong supporting evidence that the connection (in Ref. 19) between the mixed quantum-classical Liouville equation dynamics and FSSH is correct. Perhaps unsurprisingly, we find that the optimal means to produce diabatic populations from FSSH trajectories must use both surface and wavefunction information. We hope that all researchers using FSSH will benefit from this optimal transformation. More generally, we now believe that there should be far less ambiguity in the future regarding the calculation of any and all electronic properties from a swarm of surface hopping trajectories.

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