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# Estimating the entropy and quantifying the impurity of a swarm of surface-hopping trajectories: A new perspective on decoherence

Wenjun Ouyang and Joseph E. Subotnik<sup>a)</sup>

Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, USA

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In this article, we consider the intrinsic entropy of Tully's fewest switches surface hopping (FSSH) algorithm (as estimated by the impurity of the density matrix) [J. Chem. Phys. **93**, 1061 (1990)]. We show that, even for a closed system, the total impurity of a FSSH calculation increases in time (rather than stays constant). This apparent failure of the FSSH algorithm can be traced back to an incorrect, approximate treatment of the electronic coherence between wavepackets moving along different potential energy surfaces. This incorrect treatment of electronic coherence also prevents the FSSH algorithm from correctly describing wavepacket recoherences (which is a well established limitation of the FSSH method). Nevertheless, despite these limitations, the FSSH algorithm often predicts accurate observables because the electronic coherence density is modulated by a phase factor which varies rapidly in phase space and which often integrates to almost zero. Adding "decoherence" events on top of a FSSH calculation completely destroys the incorrect FSSH electronic coherence and effectively sets the Poincaré recurrence time for wavepacket recoherence to infinity; this modification usually increases FSSH accuracy (assuming there are no recoherences) while also offering long-time stability for trajectories. In practice, we show that introducing "decoherence" events does not change the total FSSH impurity significantly, but does lead to more accurate evaluations of the impurity of the electronic subsystem. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4876491>]

## I. INTRODUCTION

If the universe is governed by the laws of quantum mechanics and began originally in a pure state (with zero total entropy), then the universe must always remain in a pure state thereafter (with zero total entropy). If the universe (with  $N$  particles) is governed by the laws of classical mechanics with density  $\rho(\vec{R}, \vec{P}, 0)$  in phase space at time 0, then the total time-dependent entropy

$$S_{cl}(t) = \iint \rho(\vec{R}, \vec{P}) \log(\rho(\vec{R}, \vec{P})h^{3N}) dR^{3N} dP^{3N} \quad (1)$$

will be conserved throughout time,  $\partial S_{cl}/\partial t = 0$ . Now both of these predictions do not match up with the second law of thermodynamics. Starting with Boltzmann's celebrated H-theorem<sup>2,3</sup> there has been a great deal of literature explaining how the "effective" entropy of the entire universe tends to grow, provided that one defines the "effective" entropy as the sum of the entropy of many individual subsystems (each entangled with their surroundings). These entropic statements hold both for quantum and classical mechanics. For example, in the case of Boltzmann's H-theorem describing a dilute gas, the "effective" entropy ( $S_H$ ) that tends to grow in time (until equilibrium is reached) is the entropic integral of the reduced, one-particle distribution function:

$$f(R, P) = N \int \cdots \int \rho(R, R_2, \dots, R_{3N}, P, P_2, \dots, P_{3N}) \times dR_2 \dots dR_{3N} dP_2 \dots dP_{3N}, \quad (2)$$

<sup>a)</sup>Electronic mail: subotnik@sas.upenn.edu

$$S_H(t) = \iint f(R, P) \log(f(R, P)h) dR dP. \quad (3)$$

Because the notion of quantum entropy is different from the notion of classical entropy, the question of entropy evolution inevitably arises for mixed quantum-classical simulations. In particular, for Tully's fewest switches surface hopping (FSSH) algorithm (which is used extensively nowadays to simulate the dynamics of electronic relaxation<sup>4-11</sup>), one expects interesting questions about entropy to manifest themselves for the FSSH algorithm. After all, by treating quantum electrons separately from classical nuclei, nuclear-electronic coherence and decoherence can become fuzzy and counting states (and measuring entropy) may be nontrivial.

To our knowledge, to date there has been no standard definition for the total entropy of a FSSH calculation, much less a discussion about the role of entropy in FSSH nonadiabatic dynamics. While many researchers (including the authors) in the past have focused on "decoherence" corrections to the FSSH algorithm that aim to fix up the algorithm,<sup>5,12-27</sup> the total entropy of a FSSH calculation has not been quantified previously nor have the origins of irreversibility in FSSH dynamics been fully explored (though the question of detailed balance has been studied<sup>28,29</sup>). Given the importance of dephasing and decoherence phenomena<sup>30,31</sup> for photo-excited molecules (with a system of electrons and a bath of nuclei), we believe a thorough analysis of surface-hopping entropy is prudent, and the goal of the present paper is to provide such an analysis in detail.

To achieve this goal, we will draw heavily from a set of recent articles<sup>27,32</sup> that provide a rigorous framework for deriving approximately the FSSH algorithm starting from the Martens-Kapral mixed quantum classical Liouville equation (QCLE).<sup>33-42</sup> In particular, according to Refs. 27 and 32, there is a simple prescription for approximating the partial Wigner transform of the full nuclear-electronic density matrix starting from a swarm of FSSH trajectories. From such a prescription, we will calculate the impurity of a FSSH calculation (i.e., one minus the purity) which can serve as an approximate ‘‘FSSH entropy’’ for systems that are nearly pure.

Finally, armed with a tool to calculate impurity, we will show that total impurity is not conserved for a closed quantum system propagated by FSSH dynamics. In other words, even though a pure quantum state in a closed system should remain pure forever, the impurity of a FSSH calculation increases, as if there is always some external friction that mixes pure states and moves the system toward equilibrium. We will examine why impurity increases and how decoherence emerges in the context of partially Wigner transformed wavepackets. Inevitably, our analysis will reach back to the approximations invoked in Ref. 27. Specifically, according to Ref. 27, FSSH dynamics will approximate true QCLE dynamics provided that (i) wavepacket separation is not followed by wavepacket recoherence and (ii) the equation of motion (EOM) for the off-diagonal electronic density matrix element is modified from the original time-dependent electronic Schrödinger equation. Formally, modifying the off-diagonal EOM requires a swarm of interacting (rather than independent) FSSH trajectories, but we have argued that approximations for independent trajectories are possible (e.g., augmented fewest switches surface hopping (A-FSSH))<sup>43,44</sup>. Modification of the off-diagonal EOM is necessary to force the electronic coherences between surfaces 1 and 2 to move along the average surface – with a force  $(F_1 + F_2)/2$  – as the QCLE stipulates. (This notion of an average surface has also been discussed by many other authors.<sup>45-48</sup>) As we will show, the two approximations discussed here have consequences for the impurity (and entropy) of a FSSH calculation.

An outline of this article is as follows. In Sec. II, we review the different definitions of impurity for a Wigner wavepacket moving on one electronic surface. In Sec. III, we make a straightforward definition of impurity for a Wigner wavepacket moving along multiple electronic energy surfaces, and in Secs. III A and III B, we verify that this new definition of impurity is conserved by both the Schrödinger equation and the QCLE for a partially Wigner transformed density matrix. In Sec. III C, we define the impurity for a FSSH calculation. In Sec. IV, we present results for two model Hamiltonians together demonstrating that surface hopping methods do not conserve the total impurity of the universe. Finally in Sec. V, we rationalize this increase in impurity by studying the case of two frozen Gaussians, where an apparently mixed (i.e., not pure) density matrix arises when one ignores off-diagonal elements of the partial Wigner density matrix that oscillate rapidly in phase space. In this sense, decoherence emerges as the result of a stationary phase approximation. For a seasoned practitioner of surface hopping, who may not be

surprised to learn that FSSH dynamics do not conserve the total impurity of the universe, note that this article presents a new analytic formula for estimating FSSH impurity (in Sec. V B).

Our notation will be as follows. For indices,  $i, j, k$  label adiabatic electronic states;  $M, L, K$  label joint nuclear-electronic states;  $\alpha$  is a general nuclear coordinate;  $\mu$  and  $\eta$  are indices for a grid point in phase space. For physical quantities,  $\rho$  refers to the full nuclear-electronic density matrix;  $\Phi$  denotes an adiabatic electronic wavefunction;  $\Psi$  is a joint nuclear-electronic wavefunction;  $A_{ij}$  is the partially Wigner transformed density matrix calculated from surface hopping data; and  $A_{ij}^W$  is the exact partially Wigner transformed density matrix.

## II. BACKGROUND: THE ENTROPY OF A WIGNER WAVEPACKET ON ONE ELECTRONIC SURFACE

While there are many ways to calculate the quantum entropy,<sup>49</sup> the only approach that satisfies all of the Shannon constraints<sup>50</sup> is the von Neumann entropy:

$$S = -\text{Tr}(\rho \ln \rho), \quad (4)$$

where  $\rho$  is the quantum density matrix. Unfortunately, in practice, calculating the logarithm in Eq. (4) requires diagonalization of the density matrix, which is not realistic in general for systems with many nuclear degrees of freedom.

For this article, we would like to calculate an approximate entropy of a general Wigner wavepacket in phase space, which is a subject with a long history.<sup>49</sup> For one electronic surface, the Wigner transform is defined by

$$A^W(\vec{R}, \vec{P}, t) = \frac{1}{2\pi\hbar} \int d\vec{X} e^{i\vec{P}\cdot\vec{X}/\hbar} \left\langle \vec{R} - \frac{\vec{X}}{2} \left| \rho(t) \right| \vec{R} + \frac{\vec{X}}{2} \right\rangle. \quad (5)$$

As is well known,  $A^W(\vec{R}, \vec{P}, t)$  can take on negative values and thus, however tempting, one cannot simply apply Eq. (1) by substituting  $\rho_{cl}(\vec{R}, \vec{P}) = A^W(\vec{R}, \vec{P})$ . Of course, one could transform to the Husimi distribution, but then the equation of motion becomes significantly more complicated. As a practical matter, for a Wigner wavepacket, we require a tractable and easy means to evaluate entropy.

Beyond the von Neumann entropy, a feasible way to estimate the entropy has been proposed as one minus the purity (impurity):<sup>49,51,52</sup>

$$S(t) = 1 - (2\pi\hbar)^D \int d\vec{R} d\vec{P} (A^W(\vec{R}, \vec{P}, t))^2, \quad (6)$$

where  $D$  is the number of degrees of freedom. Eq. (6) has a number of appealing properties:

- The impurity is conserved in time according to the time-dependent Schrödinger equation.
- The impurity is 0 for pure states.
- The impurity is positive for mixed states.

Below, we will generalize Eq. (6) to the case of many electronic states, and thus evaluate the impurity of a FSSH calculation. Note that, formally, the definition of impurity in Eq. (6) is a valid approximation of the von Neumann entropy, Eq. (4), only when the universe is close to pure, so that one can expand the density matrix  $\rho = 1 - z$  in powers of  $z$ .

### III. THE IMPURITY OF A PARTIAL WIGNER WAVEPACKET ON MULTIPLE ELECTRONIC SURFACES

For a physical problem with multiple potential energy surfaces (PESs), the partially Wigner transformed density matrix is<sup>40,41</sup>

$$A_{ij}^W(\vec{R}, \vec{P}, t) \equiv \left(\frac{1}{2\pi\hbar}\right)^{3N} \int d\vec{X} e^{i\vec{P}\cdot\vec{X}/\hbar} \times \left\langle \Phi_i(\vec{R}); \vec{R} - \frac{\vec{X}}{2} \left| \rho(t) \right| \Phi_j(\vec{R}); \vec{R} + \frac{\vec{X}}{2} \right\rangle, \quad (7)$$

where  $\{|\Phi_i(\vec{R})\rangle\}$  are the basis of adiabatic electronic wavefunctions at nuclear position  $\vec{R}$  and  $N$  is the number of nuclei. In this case, the natural extension of Eq. (6) is to calculate the

impurity as

$$S(t) \equiv 1 - (2\pi\hbar)^{3N} \int d\vec{R} \int d\vec{P} \text{Tr}(\mathbf{A}^W(\vec{R}, \vec{P}, t)^2) \\ = 1 - (2\pi\hbar)^{3N} \sum_{i,j} \int d\vec{R} \int d\vec{P} A_{ij}^W(\vec{R}, \vec{P}, t) \cdot A_{ji}^W(\vec{R}, \vec{P}, t). \quad (8)$$

### A. Exact dynamics from the Schrödinger equation

To prove that Eq. (8) is a meaningful definition of impurity for a system with several accessible electronic states, we must first prove that, according to this definition, impurity is conserved in time when a closed system is propagated by the Schrödinger equation. To prove this fact, one starts from a density matrix

$$\rho = \sum_{K=1}^{N_K} b_K |\Psi_K(t)\rangle \langle \Psi_K(t)|. \quad (9)$$

In principle,  $\rho$  can represent a pure state ( $N_K = 1$ ) or a mixed state ( $N_K > 1$ ). The set  $\{|\Psi_K(t)\rangle\}$  here denotes a basis of orthonormal, fully coupled nuclear-electronic wavefunctions. By substituting Eq. (9) into Eq. (7) and using the identity  $\int d\vec{P} e^{i\vec{P}\cdot\vec{X}} = (2\pi)^{3N} \delta(\vec{X})$ , one can calculate the impurity in Eq. (8):

$$S(t) = 1 - (2\pi\hbar)^{-3N} \sum_{M,L} b_M b_L \int d\vec{P} \int d\vec{R} \sum_{i,j} \int d\vec{X} \int d\vec{Y} e^{i\vec{P}\cdot(\vec{X}+\vec{Y})/\hbar} \left\langle \Phi_i(\vec{R}); \vec{R} - \frac{\vec{X}}{2} \left| \Psi_M(t) \right\rangle \right. \\ \times \left\langle \Psi_M(t) \left| \Phi_j(\vec{R}); \vec{R} + \frac{\vec{X}}{2} \right\rangle \left\langle \Phi_j(\vec{R}); \vec{R} - \frac{\vec{Y}}{2} \left| \Psi_L(t) \right\rangle \left\langle \Psi_L(t) \left| \Phi_i(\vec{R}); \vec{R} + \frac{\vec{Y}}{2} \right\rangle \right. \\ = 1 - \sum_{M,L} b_M b_L \int d\vec{R} \sum_{i,j} \int d\vec{X} \int d\vec{Y} \delta(\vec{X} + \vec{Y}) \left\langle \Phi_i(\vec{R}); \vec{R} - \frac{\vec{X}}{2} \left| \Psi_M(t) \right\rangle \right. \\ \times \left\langle \Psi_M(t) \left| \Phi_j(\vec{R}); \vec{R} + \frac{\vec{X}}{2} \right\rangle \left\langle \Phi_j(\vec{R}); \vec{R} - \frac{\vec{Y}}{2} \left| \Psi_L(t) \right\rangle \left\langle \Psi_L(t) \left| \Phi_i(\vec{R}); \vec{R} + \frac{\vec{Y}}{2} \right\rangle \right. \\ = 1 - \sum_{M,L} b_M b_L \int d\vec{R} \int d\vec{X} \left( \sum_i \left\langle \Phi_i(\vec{R}); \vec{R} - \frac{\vec{X}}{2} \left| \Psi_M(t) \right\rangle \left\langle \Psi_L(t) \left| \Phi_i(\vec{R}); \vec{R} - \frac{\vec{X}}{2} \right\rangle \right) \right. \\ \times \left( \sum_j \left\langle \Phi_j(\vec{R}); \vec{R} + \frac{\vec{X}}{2} \left| \Psi_L(t) \right\rangle \left\langle \Psi_M(t) \left| \Phi_j(\vec{R}); \vec{R} + \frac{\vec{X}}{2} \right\rangle \right). \quad (10)$$

Now, using the fact that the set of adiabatic electronic eigenstates  $\{|\Phi_i(\vec{R})\rangle\}$  is complete, so that an electronic trace is invariant to the nuclear position associated with the adiabats,

$$S(t) = 1 - \sum_{M,L} b_M b_L \int d\vec{R} \int d\vec{X} \text{Tr}_e \left[ \left\langle \vec{R} - \frac{\vec{X}}{2} \left| \Psi_M(t) \right\rangle \left\langle \Psi_L(t) \left| \vec{R} - \frac{\vec{X}}{2} \right\rangle \right] \right. \\ \times \text{Tr}_e \left[ \left\langle \vec{R} + \frac{\vec{X}}{2} \left| \Psi_L(t) \right\rangle \left\langle \Psi_M(t) \left| \vec{R} + \frac{\vec{X}}{2} \right\rangle \right], \quad (11)$$

where  $\text{Tr}_e$  signifies a trace over electronic states. Now, switching variables to

$$\begin{aligned}\bar{\omega}_1 &= \bar{R} + \frac{\bar{X}}{2}, & \bar{\omega}_2 &= \bar{R} - \frac{\bar{X}}{2}, \\ \int d\bar{R} \int d\bar{X} &\rightarrow \int d\bar{\omega}_2 \int d\bar{\omega}_1,\end{aligned}\quad (12)$$

we find that the expression for impurity reduces to

$$\begin{aligned}S(t) &= 1 - \sum_{M,L} b_M b_L \text{Tr}_e \text{Tr}_n [|\Psi_M(t)\rangle \langle \Psi_L(t)|] \\ &\quad \times \text{Tr}_e \text{Tr}_n [|\Psi_L(t)\rangle \langle \Psi_M(t)|] \\ &= 1 - \sum_{M,L} b_M b_L |\langle \Psi_M(t) | \Psi_L(t) \rangle|^2 \\ &= 1 - \sum_M b_M^2,\end{aligned}\quad (13)$$

where  $\text{Tr}_n$  is the trace over nuclei. Thus, in the end, the impurity according to Eq. (8) is clearly time independent and satisfies our intrinsic notation of impurity: it is zero for pure states and positive for mixed states. Note that, in Eq. (13),  $S(t)$  is in fact identical to the fully quantum mechanical impurity,  $S(t) = 1 - \text{Tr}(\rho^2)$ . This agreement between the semiclassical and quantum mechanical impurities arises only because the impurity in Eq. (8) is second order in the density matrix. More generally, we are unaware of a simple semiclassical formula to estimate even  $\text{Tr}(\rho^4)$  (much less  $\text{Tr}(\rho \ln \rho)$ ) starting from the Wigner representation.

## B. The quantum-classical Liouville equation

Having proved that the impurity in Eq. (8) is conserved according to exact quantum dynamics, we can show that the impurity of Eq. (8) is also conserved in time exactly by the QCLE. To prove this statement, note that the time derivative of the impurity is

$$\begin{aligned}\frac{\partial S}{\partial t} &= -(2\pi\hbar)^{3N} \sum_{i,j} \int d\bar{R} \int d\bar{P} \left\{ \frac{\partial}{\partial t} A_{ij}^W(\bar{R}, \bar{P}, t) \cdot A_{ji}^W(\bar{R}, \bar{P}, t) + A_{ij}^W(\bar{R}, \bar{P}, t) \cdot \frac{\partial}{\partial t} A_{ji}^W(\bar{R}, \bar{P}, t) \right\} \\ &= -(2\pi\hbar)^{3N} \sum_{i,j} 2 \int d\bar{R} \int d\bar{P} \text{Re} \left( \frac{\partial}{\partial t} A_{ij}^W(\bar{R}, \bar{P}, t) \cdot A_{ji}^W(\bar{R}, \bar{P}, t) \right).\end{aligned}\quad (14)$$

According to the QCLE, the partially Wigner transformed density matrix evolves according to

$$\frac{\partial}{\partial t} A_{ij}^W(\bar{R}, \bar{P}, t) = \frac{-i}{\hbar} \sum_k (V_{ik} A_{kj}^W - A_{ik}^W V_{kj}) - \sum_{k,\alpha} \frac{P^\alpha}{M^\alpha} (d_{ik}^\alpha A_{kj}^W - A_{ik}^W d_{kj}^\alpha) - \sum_\alpha \frac{P^\alpha}{M^\alpha} \frac{\partial A_{ij}^W}{\partial R^\alpha} - \frac{1}{2} \sum_{k,\alpha} \left( F_{ik}^\alpha \frac{\partial A_{kj}^W}{\partial P^\alpha} + \frac{\partial A_{ik}^W}{\partial P^\alpha} F_{kj}^\alpha \right).\quad (15)$$

When we substitute Eq. (15) into Eq. (14), we find that

$$\begin{aligned}\frac{\partial S}{\partial t} &= (2\pi\hbar)^{3N} \int_{-\infty}^{\infty} d\bar{R} \int_{-\infty}^{\infty} d\bar{P} \text{Re} \left[ \frac{2i}{\hbar} \sum_{i,j,k} (V_{ik} A_{kj}^W A_{ji}^W - A_{ik}^W V_{kj} A_{ji}^W) + \sum_{i,j,k,\alpha} \frac{2P^\alpha}{M^\alpha} (d_{ik}^\alpha A_{kj}^W A_{ji}^W - A_{ik}^W d_{kj}^\alpha A_{ji}^W) \right. \\ &\quad \left. + \sum_{i,j,\alpha} \frac{2P^\alpha}{M^\alpha} \frac{\partial A_{ij}^W}{\partial R^\alpha} A_{ji}^W + \sum_{i,j,k,\alpha} \left( F_{ik}^\alpha \frac{\partial A_{kj}^W}{\partial P^\alpha} A_{ji}^W + \frac{\partial A_{ik}^W}{\partial P^\alpha} F_{kj}^\alpha A_{ji}^W \right) \right] \\ &= (2\pi\hbar)^{3N} \int_{-\infty}^{\infty} d\bar{R} \int_{-\infty}^{\infty} d\bar{P} \text{Re} \left[ \frac{2i}{\hbar} \sum_{i,j} ((V_{ii} - V_{jj}) |A_{ij}^W|^2) + \sum_\alpha \frac{2P^\alpha}{M^\alpha} \left( \sum_{i,j,k} d_{ik}^\alpha A_{kj}^W A_{ji}^W - \sum_{i,j,k} A_{ik}^W d_{kj}^\alpha A_{ji}^W \right) \right. \\ &\quad \left. + \sum_{i,j,\alpha} \frac{2P^\alpha}{M^\alpha} \frac{\partial A_{ij}^W}{\partial R^\alpha} A_{ji}^W + \sum_\alpha \left( \sum_{i,j,k} F_{ik}^\alpha \frac{\partial A_{kj}^W}{\partial P^\alpha} A_{ji}^W + \sum_{i,j,k} \frac{\partial A_{ik}^W}{\partial P^\alpha} F_{kj}^\alpha A_{ji}^W \right) \right].\end{aligned}\quad (16)$$

The first two terms are clearly zero (because there is no real part). Now for the third and sixth terms, by changing the summation index  $\{i, j, k\} \rightarrow \{k, i, j\}$ , one finds

$$\begin{aligned} \frac{\partial S}{\partial t} &= (2\pi\hbar)^{3N} \int_{-\infty}^{\infty} d\vec{R} \int_{-\infty}^{\infty} d\vec{P} \operatorname{Re} \left[ \sum_{\alpha} \frac{2P^{\alpha}}{M^{\alpha}} \left( \sum_{k,i,j} d_{kj}^{\alpha} A_{ji}^W A_{ik}^W - \sum_{i,j,k} A_{ik}^W d_{kj}^{\alpha} A_{ji}^W \right) \right. \\ &\quad \left. + \sum_{i,j,\alpha} \frac{2P^{\alpha}}{M^{\alpha}} \frac{\partial A_{ij}^W}{\partial R^{\alpha}} A_{ji}^W + \sum_{\alpha} \left( \sum_{k,i,j} F_{kj}^{\alpha} \frac{\partial A_{ji}^W}{\partial P^{\alpha}} A_{ik}^W + \sum_{i,j,k} \frac{\partial A_{ik}^W}{\partial P^{\alpha}} F_{kj}^{\alpha} A_{ji}^W \right) \right] \\ &= (2\pi\hbar)^{3N} \sum_{i,j,k,\alpha} \int_{-\infty}^{\infty} d\vec{R} \int_{-\infty}^{\infty} d\vec{P} \left[ \frac{\partial}{\partial R^{\alpha}} \left( \frac{P^{\alpha}}{M^{\alpha}} A_{ij}^W A_{ji}^W \right) + \frac{\partial}{\partial P^{\alpha}} \left( A_{ik}^W F_{kj}^{\alpha} A_{ji}^W \right) \right] \\ &= 0. \end{aligned} \quad (17)$$

In the last equality, we assume that the density matrix decays to zero sufficiently fast (as it must for any closed system). Thus, the impurity of a partially transformed Wigner wavepacket is conserved in time according to the QCLE. This exact conservation of impurity is somewhat not obvious since the QCLE itself is an approximation of the quantum Liouville equation. In the future, it might prove interesting to explore the time evolution of the true von Neumann entropy defined in Eq. (4) (rather than the impurity) according to the QCLE; such an investigation would necessarily be more complicated than the present article.

### C. FSSH algorithm and the calculation of impurity

Let us now describe how to evaluate Eq. (8) with data computed from a surface hopping simulation. Without loss of generality, we will restrict ourselves to a system with two electronic states and one spatial dimension. For a typical surface hopping calculation, one is given a swarm of  $N_s$  trajectories, each trajectory carrying an active surface variable  $\lambda = 1, 2$  (specifying nuclear motion) and a set of electronic amplitudes  $(c_1, c_2)$ . The partial Wigner transform with elements  $A_{11}(R, P, t)$ ,  $A_{22}(R, P, t)$ , and  $A_{12}(R, P, t)$  are constructed as follows:<sup>32</sup>

$$A_{ii}(R, P, t) = \frac{1}{N_s} \sum_l \delta(R - R^l(t)) \delta(P - P^l(t)) \delta_{i,\lambda^l(t)}, \quad (18)$$

$$A_{ij}(R, P, t) = \frac{1}{N_s} \sum_l \delta(R - R^l(t)) \delta(P - P^l(t)) \sigma_{ij}^l. \quad (19)$$

Here,  $l$  is the label for each trajectory and  $\sigma_{ij}$  is defined as  $c_i c_j^*$ . Note that Eq. (19) is not unique (according to Ref. 32) but, in our experience, it has been the most numerically stable. Finally, we can calculate the impurity with Eq. (8) as

$$\begin{aligned} S(t) &= 1 - 2\pi\hbar \int dR \int dP (A_{11}(R, P, t)^2 \\ &\quad + 2|A_{12}(R, P, t)|^2 + A_{22}(R, P, t)^2). \end{aligned} \quad (20)$$

In practice, special care must be taken when evaluating the impurity above because the sum must be evaluated on a

finite grid in phase space, with the grid sizes  $\Delta R$  and  $\Delta P$ . Let  $[R_{min}, R_{min} + \Delta R, \dots, R_{max} - \Delta R, R_{max}]$  be a grid in position-space, and  $[P_{min}, P_{min} + \Delta P, \dots, P_{max} - \Delta P, P_{max}]$  be a grid in momentum-space. Then, we evaluate the partial Wigner transform at a grid point  $(R_{\mu}, P_{\eta})$  by

$$\begin{aligned} A_{ii}(R_{\mu}, P_{\eta}, t) &= \frac{1}{N_s} \sum_l \Theta \left( \frac{\Delta R}{2} - |R^l(t) - R_{\mu}| \right) \\ &\quad \times \Theta \left( \frac{\Delta P}{2} - |P^l(t) - P_{\eta}| \right), \end{aligned} \quad (21)$$

$$\begin{aligned} A_{ij}(R_{\mu}, P_{\eta}, t) &= \frac{1}{N_s} \sum_l \Theta \left( \frac{\Delta R}{2} - |R^l(t) - R_{\mu}| \right) \\ &\quad \times \Theta \left( \frac{\Delta P}{2} - |P^l(t) - P_{\eta}| \right) \sigma_{ij}^l, \end{aligned} \quad (22)$$

where  $\Theta(x)$  is the Heaviside step function. The impurity is then

$$\begin{aligned} S(t) &= 1 - 2\pi\hbar \sum_{\mu,\eta} (A_{11}(R_{\mu}, P_{\eta}, t)^2 + 2|A_{12}(R_{\mu}, P_{\eta}, t)|^2 \\ &\quad + A_{22}(R_{\mu}, P_{\eta}, t)^2) \Delta R \Delta P. \end{aligned} \quad (23)$$

Unfortunately, this procedure can be sensitive to the choice of grid size. On the one hand, if  $\Delta R$  and  $\Delta P$  are too large, the entire wavepacket can be averaged into one big bin so one does not recover the continuous integral in Eq. (20). On the other hand, if  $\Delta R$  and  $\Delta P$  are too small and we do not have enough trajectories, some bins will contain zero data points because of incomplete sampling, and our final distribution will appear scattered and distorted. We have done our best to converge our results to the correct impurity, using 40 000 trajectories.

## IV. RESULTS

To test our approach above, we investigate two standard one-dimensional problems from Tully's original paper,<sup>1</sup> the simple avoided crossing and the problem of extended

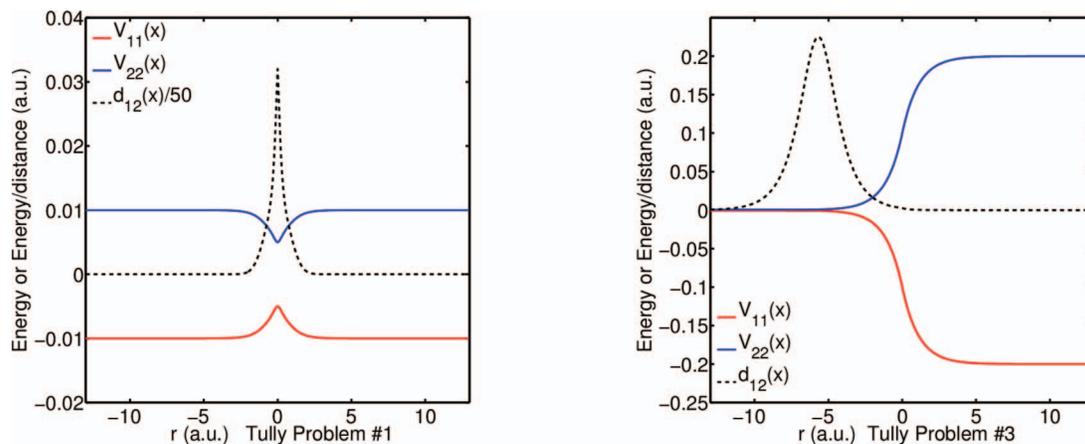


FIG. 1. The adiabatic PESs for the two standard one-dimensional problems in Tully's original paper.<sup>1</sup>

coupling. The adiabatic PESs of the two problems are shown in Fig. 1. We study two different variations of surface hopping: (1) Tully's original FSSH and (2) our group's decoherence-improved A-FSSH algorithm.<sup>43,44</sup> The A-FSSH algorithm was designed to build collapsing events on top of FSSH dynamics in order to better simulate wavepacket separation and decoherence from the perspective of the electronic subsystem following the pioneering work of Prezhd, <sup>15</sup> Rossky, <sup>13,14,21,22</sup> Hammes-Schiffer, <sup>17</sup> Truhlar, <sup>18–20,23–25</sup> and Schwartz. <sup>53,54</sup> In other words, A-FSSH was designed to better estimate the reduced electronic density matrix

$$\sigma_e(t) = \int \int d\vec{R} d\vec{P} \vec{A}(\vec{R}, \vec{P}, t) = \begin{pmatrix} \sigma_{11}(t) & \sigma_{12}(t) \\ \sigma_{21}(t) & \sigma_{22}(t) \end{pmatrix} \quad (24)$$

with corresponding electronic impurity

$$S_e(t) = 1 - \text{Tr}_e(\sigma_e^2(t)) \quad (25)$$

assuming that nuclear wavepackets on different surfaces separate irreversibly.

At time zero, we prepare a Gaussian wavepacket far to the left ( $x = -15$  a.u.) of the scattering region, starting off on the lower adiabatic PES with width  $\sigma = 1$  and a momentum of positive 20 a.u. The particle mass is 2000 a.u. We transform to the Wigner representation in phase space to initialize a swarm of surface hopping trajectories. At a set of different times, we take snapshots of the swarm of trajectories, digest the corresponding trajectory information into the phase-space grids discussed above, and then compute the impurity. For reasons of intuition, we also plot the partial Wigner distribution in phase space for two separate times: (i) right after a wavepacket is spawned and the wavepackets are still close to the coupling region, and (ii) at long times, when the wavepackets are already far removed from the coupling region.

### A. Tully problem #1: Avoided crossing

For Tully problem #1, the electronic Hamiltonian in a diabatic basis is<sup>1</sup>

$$\begin{aligned} V_{11}(x) &= A[1 - \exp(-Bx)], \quad x > 0, \\ V_{11}(x) &= -A[1 - \exp(Bx)], \quad x < 0, \\ V_{22}(x) &= -V_{11}(x), \\ V_{12}(x) &= V_{21}(x) = C \exp(-Dx^2), \end{aligned} \quad (26)$$

where  $A = 0.01$ ,  $B = 1.6$ ,  $C = 0.005$ , and  $D = 1.0$ , all in atomic units (see Fig. 1 for a picture).

For this problem, the dynamics are simple: a wavepacket enters the coupling region on the lower adiabat and spawns a new wavefunction on the upper adiabat. Eventually, two wavepackets emerge from the coupling region—both propagating forward (in the positive  $x$  direction).

In Figs. 2–5, we plot the elements of the partially Wigner transformed density matrix for surface hopping calculations

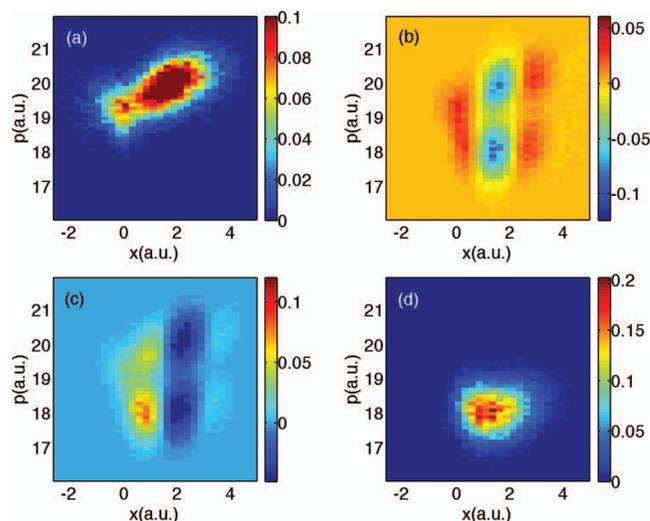


FIG. 2. FSSH data for Tully #1. The densities are plotted in phase space at time 1590 a.u., (a) top-left  $A_{11}$ ; (b) top-right  $\text{Re}(A_{12})$ ; (c) bottom-left  $\text{Im}(A_{12})$ ; and (d) bottom-right  $A_{22}$ .

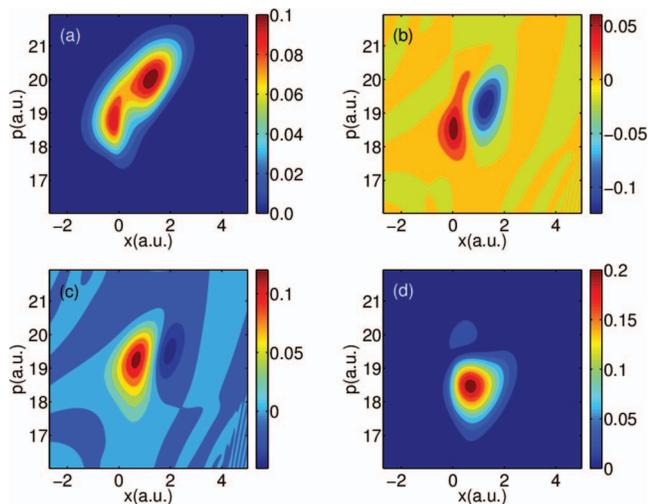


FIG. 3. Exact quantum dynamics for Tully #1: Time is 1590 a.u. Same notation as in Fig. 2. Note that FSSH data and exact data agree qualitatively for populations but not for coherences.

versus exact quantum dynamics. Here, we use FSSH surface hopping dynamics; note that A-FSSH and FSSH are almost identical here. The data are plotted at short and long times after the crossing event.

From the data, we see that the FSSH and exact results for the populations  $A_{11}^W$  and  $A_{22}^W$  agree quite well at all times. However, the FSSH algorithm only partially recovers the correct form for  $A_{12}^W$ . Whereas exact quantum dynamics predicts only two peaks (one positive, the other negative) for the coherence, FSSH predicts multiple peaks that are correlated with the diagonal peaks. The agreement gets worse for long times. According to exact quantum dynamics, there are also small oscillations in phase for the off-diagonal matrix elements that are absent for FSSH dynamics. These observations will be explained in detail.

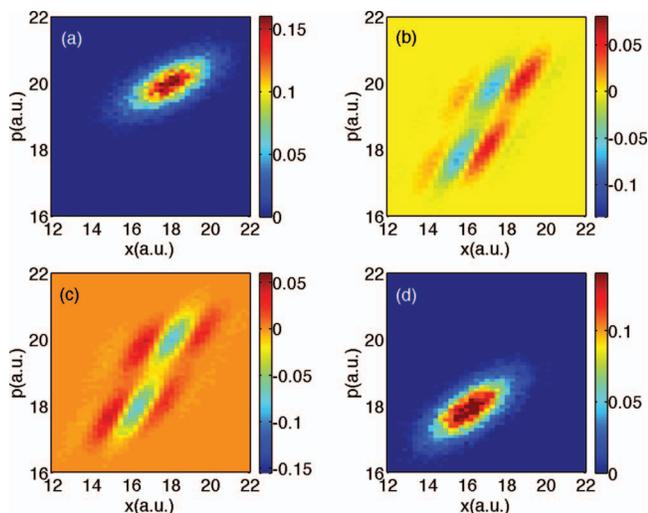


FIG. 4. FSSH data for Tully #1: Time is 3300 a.u. Same notation as in Fig. 2.

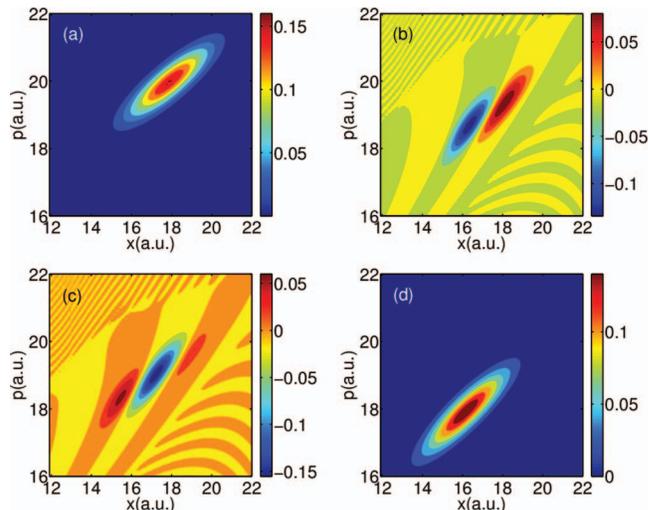


FIG. 5. Exact quantum dynamics for Tully #1: Time is 3300 a.u. Same notation as in Fig. 2. Note that FSSH data and exact data agree qualitatively for populations but not for coherences.

## B. Tully problem #3: Extended couplings

For Tully problem #3, the electronic Hamiltonian in a diabatic basis is<sup>1</sup>

$$\begin{aligned} V_{11}(x) &= -A, \\ V_{22}(x) &= A, \\ V_{12}(x) &= B \exp(Cx), \quad x < 0, \\ V_{12}(x) &= B[2 - \exp(-Cx)], \quad x > 0, \end{aligned} \quad (27)$$

where  $A = 0.0006$ ,  $B = 0.1$ , and  $C = 0.9$ , all in atomic units (see Fig. 1 for a picture).

For this model Hamiltonian, the dynamics are more complicated than the previous problem. Here, one wavepacket begins far to the left on the lower adiabat and, moving to the right, a second wavepacket is spawned on the upper adiabat. Afterwards, the two wavepackets continue moving right and leave the coupling region. At time 1650 a.u., the wavepacket on the lower adiabat is moving quickly to the right and eventually it will transmit with nearly 100% probability. At the same time, the wavepacket on the upper adiabat has slowed down and is in the process of turning around; this wavepacket will reflect with nearly 100% probability. Later on, before time  $t = 3300$  a.u., the reflecting wavepacket on the upper adiabat will spawn another wavepacket on the lower adiabat, and both of these wavepackets will then move together to the left asymptotically.

In Figs. 6–8, we plot results for A-FSSH, FSSH, and exact quantum dynamics at time 1650 a.u., not long after the spawning event. Note that the population data from FSSH and A-FSSH track the exact quantum dynamics data nearly quantitatively. However, at the same time, we see that the off-diagonal matrix elements could not be more different. In particular, according to exact quantum dynamics, the  $A_{12}^W$  coherence matrix element is centered midway between the  $A_{11}^W$  and  $A_{22}^W$  population matrix elements. By contrast, FSSH predicts that the coherences should be centered on the population peak positions (just as for Tully problem #1). At the same time,

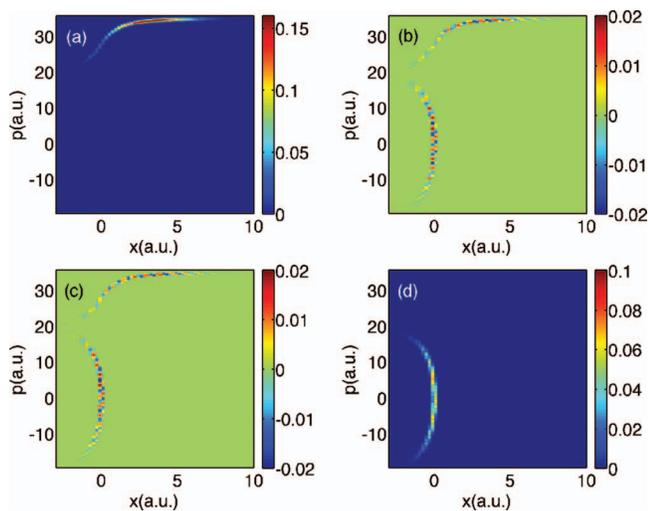


FIG. 6. FSSH data for Tully #3: Time is 1650 a.u. Same notation as in Fig. 2.

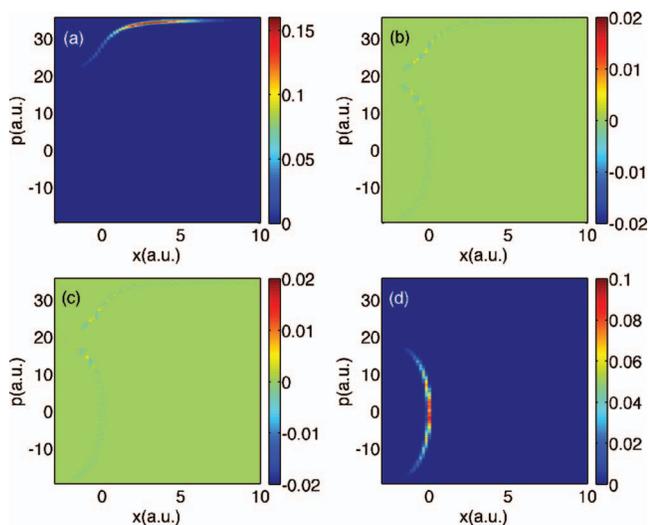


FIG. 7. A-FSSH data for Tully #3: Time is 1650 a.u. Same notation as in Fig. 2.

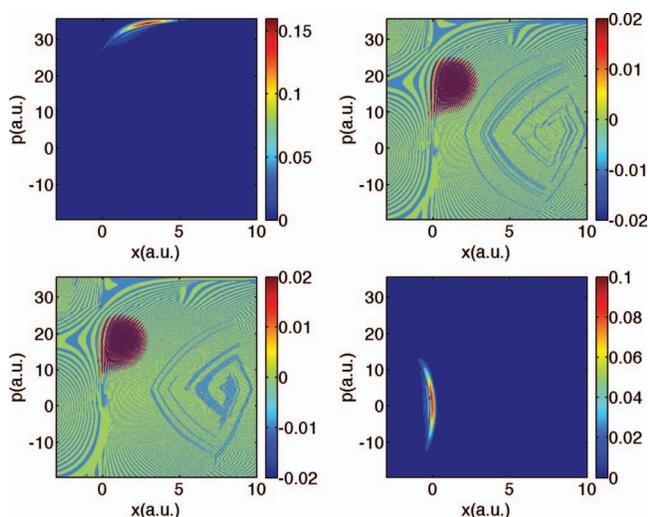


FIG. 8. Exact quantum dynamics data for Tully #3: Time is 1650 a.u. Same notation as in Fig. 2.

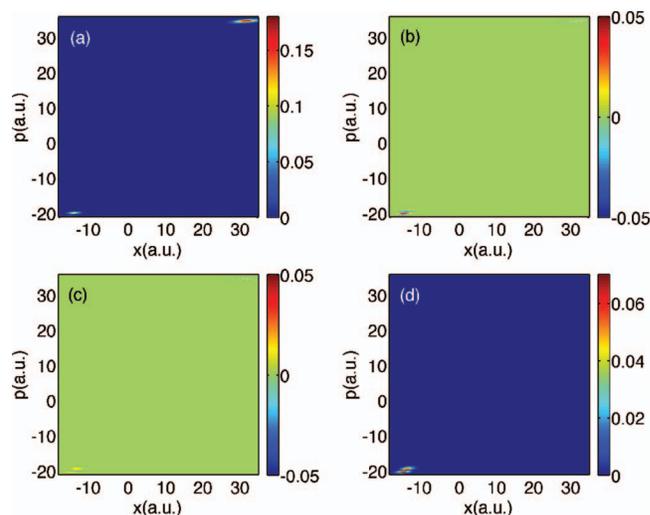


FIG. 9. FSSH data for Tully #3: Time is 3300 a.u. Same notation as in Fig. 2.

because of a collapsing event triggered by wavepacket separation, A-FSSH predicts almost exactly zero coherence.

Finally, for long times ( $t = 3300$  a.u.), we plot all data in Figs. 9–11. Focusing first on populations, exact quantum dynamics reveals a small peak in between the two centers of populations around  $(x, p) \approx (5, 5)$ ; this feature is absent from the surface hopping data and will be explained in Sec. V A. Otherwise, the surface hopping data look qualitatively correct.

With regards to the coherences in Figs. 9–11, exact quantum dynamics predicts that the off-diagonal matrix element is incredibly small except for a small peak midway between the two population centers at  $(x, p) \approx (5, 5)$  and phase oscillations are observed around that peak. Neither A-FSSH nor FSSH find such a peak nor such oscillations; these features will also be explained below.

Interestingly, notice that, if one looks at  $A_{12}$  in Fig. 9 around the transmitting peak at  $(x, p) = (30, 45)$ , the FSSH decoherence problem is barely visible. In fact, the FSSH

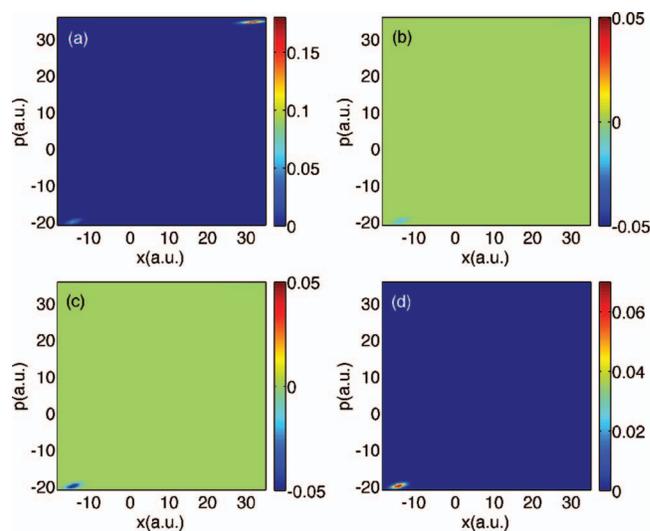


FIG. 10. A-FSSH data for Tully #3: Time is 3300 a.u. Same notation as in Fig. 2.

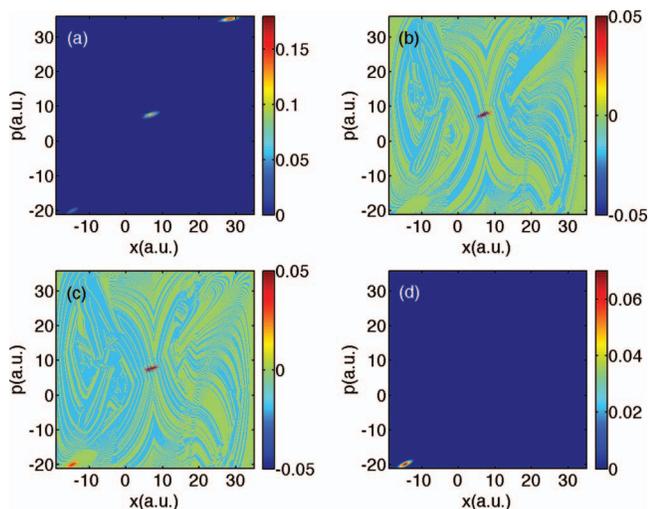


FIG. 11. Exact quantum dynamics data for Tully #3: Time is 3300 a.u. Same notation as in Fig. 2.

coherence density appears almost as small as the A-FSSH coherence density, even though we know that, for this specific problem, the FSSH methodology breaks down;<sup>15,53</sup> unlike A-FSSH, the FSSH algorithm fails to account for the bifurcation between transmitting and reflecting wavefunctions. To explain this surprising feature, recall that, for these figures, we are averaging over finite chunks of phase space; as we have explained in Ref. 55, Tully problem #3 is pathological because, by chance, averaging removes FSSH's decoherence problems. To prove that the FSSH coherences are actually large and that the data scale in Fig. 9 is small only by a fortuitous cancellation of sign, in Fig. 12 we plot the function:

$$A_{12}^{norm}(R, P, t) \equiv \frac{1}{N_s} \sum_l \delta(R - R^l(t)) \delta(P - P^l(t)) |\sigma_{ij}^l|. \quad (28)$$

From Fig. 12, it is clear that each FSSH trajectory carries an electronic density matrix with a large off-diagonal component, and the FSSH algorithm does well only because averaging over a phase space volume allows for a fortuitous sign cancellation.<sup>55</sup>

### C. Impurity

Having analyzed the capacity of surface hopping methods to recover the partial Wigner transform densities in phase space, in Fig. 13 we plot the total impurity ( $S(t)$ , Eq. (20)) as function of time both for FSSH and A-FSSH trajectories. Here,  $\Delta R$  and  $\Delta P$  are chosen by insisting that the total impurity be zero at time zero, and we have checked that our data are changed only slightly by altering the grid sizes.

According to Fig. 13, we find that the total impurity grows in time for both FSSH and A-FSSH as soon as particles start hopping in between surfaces. As we will show in Sec. V B, one can evaluate this growth in total impurity analytically for simple problems (e.g., for Tully #1). From the data in Secs. IV A and IV B, it is clear that this growth in total impurity can be attributed to the off-diagonal errors of FSSH.

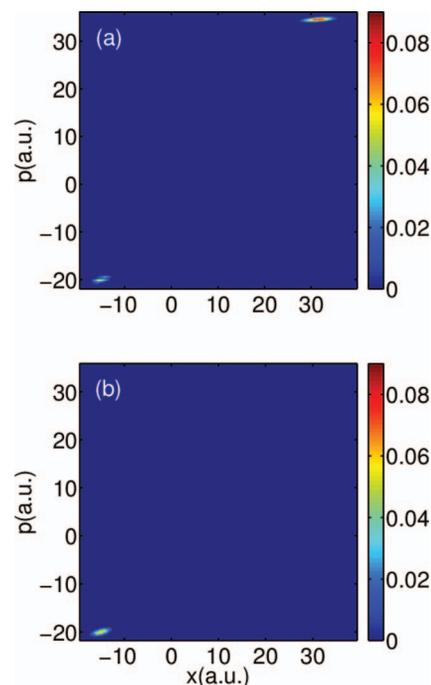


FIG. 12. FSSH and A-FSSH data for Tully #3. Here, we evaluated the absolute value of the coherence, i.e., Eq. (28) and time is 3300 a.u. (a) FSSH and (b) A-FSSH.

Interestingly, according to Fig. 13, even though A-FSSH incorporates decoherence, FSSH and A-FSSH yield very similar total impurities. This coincidence can be explained by the simple fact that neither algorithm captures the exact coherence and neither can correctly recover recoherences. The premise of the A-FSSH algorithm is that, since recoherences cannot be captured correctly by any Tully-style surface

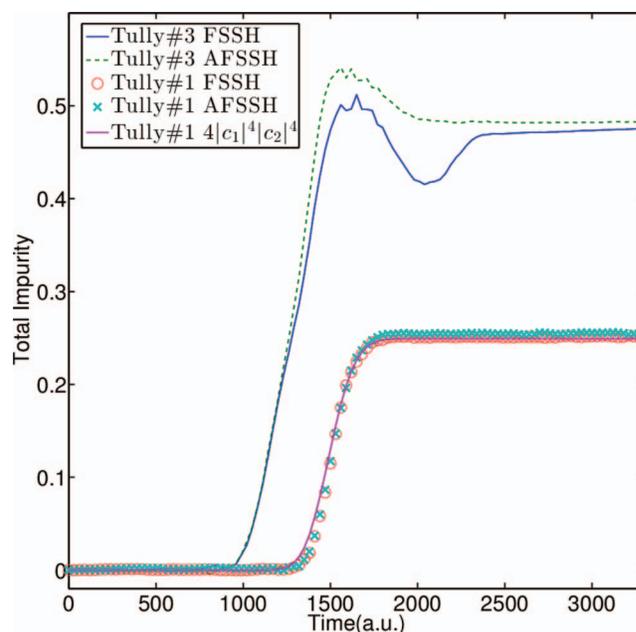


FIG. 13. The total impurity  $S(t)$  from Eq. (20) for the FSSH and A-FSSH algorithms for Tully problems #1 and #3. We also plot Eq. (42), an approximate analytical result for frozen Gaussians. The total impurity of the exact quantum system is zero for all time.

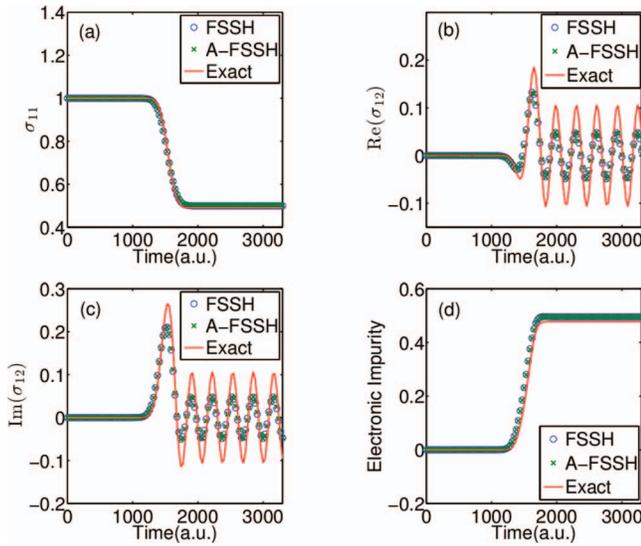


FIG. 14. The reduced electronic density matrix for Tully problem #1 according to exact quantum dynamics, FSSH, and A-FSSH. (a)  $\sigma_{11}$ ; (b)  $\text{Re}(\sigma_{12})$ ; (c)  $\text{Im}(\sigma_{12})$ ; and (d) the electronic impurity  $S_e(t)$  (Eq. (25)). (a), (b), and (c) are expressed in the diabatic basis. Note that the electronic impurity increases, and both FSSH and A-FSSH recover the correct electronic impurity.

hopping algorithm, one should damp the electronic coherences after wavepackets separate so that long time dynamics (without recoherences) will be stable and accurate.<sup>56</sup> In other words, A-FSSH was designed to recover the correct impurity of the electronic subsystem (which is entangled with the nuclei).

To prove that A-FSSH delivers on this promise, we plot the elements of reduced electronic density matrix and electronic impurity ( $S_e(t)$ , Eq. (25)) in Figs. 14 and 15. From the figures, we observe that A-FSSH recovers qualitatively the exact reduced electronic density matrix for Tully problem #1 and quantitatively the exact reduced electronic density ma-

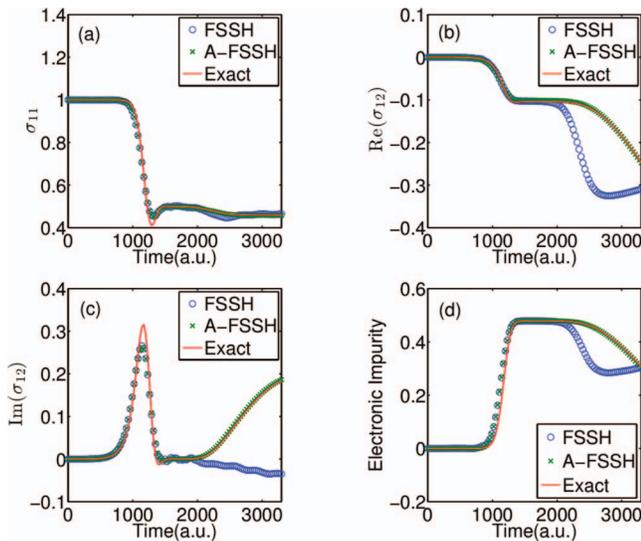


FIG. 15. The reduced electronic density matrix for Tully problem #3 according to exact quantum dynamics, FSSH, and A-FSSH. (a)  $\sigma_{11}$ ; (b)  $\text{Re}(\sigma_{12})$ ; (c)  $\text{Im}(\sigma_{12})$ ; and (d) the electronic impurity  $S_e(t)$  (Eq. (25)). (a), (b), and (c) are expressed in the diabatic basis. Note that only A-FSSH recovers the correct electronic impurity.

trix for Tully problem #3. Moreover, in both cases, A-FSSH exactly reproduces the impurity of the electronic subsystem (which grows in time as would be expected). Note that FSSH recovers neither the correct reduced electronic density matrix nor the electronic impurity for Tully problem #3.

## V. DISCUSSION: FROZEN GAUSSIAN DYNAMICS IN A PARTIALLY TRANSFORMED WIGNER PHASE SPACE

### A. Exact quantum dynamics predicts nonlocal coherences and phase oscillations

The data in Secs. IV A and IV B highlighted the fact the surface hopping dynamics can recover the populations well (compared to the exact partial Wigner transform), but off-diagonal coherences are not as accurate. These results should not be very surprising to a reader familiar with Ref. 27, where it was shown that (i) the on-diagonal equations of motion for FSSH are almost exactly the same as the corresponding QCLE equations of motion; but (ii) the off-diagonal equations of motion for FSSH need a severe correction to approximate the corresponding QCLE equations of motion. And formally, these corrections require interacting (rather than independent) trajectories. In the present paper, we have seen that the FSSH errors in off-diagonal coherence lead effectively to a growth in total impurity over time.

To better interpret our data from Secs. IV A and IV B, we will now find it useful to investigate wavepacket bifurcation in phase space from the perspective of frozen Gaussian nonadiabatic dynamics. With a frozen Gaussian ansatz, the total nuclear-electronic wavefunction has the following form:<sup>27</sup>

$$\Psi(\vec{r}, \vec{R}, t) = c_1 g(\vec{R}; \vec{R}_1(t), \vec{P}_1(t)) \Phi_1(\vec{r}; \vec{R}) + c_2 g(\vec{R}; \vec{R}_2(t), \vec{P}_2(t)) \Phi_2(\vec{r}; \vec{R}), \quad (29)$$

where  $g$  represents a nuclear Gaussian wavepacket

$$g(\vec{R}; \vec{R}_s(t), \vec{P}_s(t)) \equiv \prod_{\alpha} \left( \frac{1}{\pi a_{R^{\alpha}}^2} \right)^{1/4} \exp \left( \frac{-(R^{\alpha} - R_s^{\alpha}(t))^2}{2a_{R^{\alpha}}^2} \right) \times \exp \left( \frac{i}{\hbar} P_s^{\alpha}(t) (R^{\alpha} - R_s^{\alpha}(t)) \right). \quad (30)$$

According to Eq. (7), the partial Wigner transform for a frozen Gaussian is (for  $i = 1, 2$ )

$$A_{11}^W(\vec{R}, \vec{P}) = \frac{|c_1|^2}{(\pi \hbar)^{3N}} \prod_{\alpha} \exp \left( \frac{-(R^{\alpha} - R_1^{\alpha})^2}{a_{R^{\alpha}}^2} \right) \times \exp \left( \frac{-(P^{\alpha} - P_1^{\alpha})^2 a_{R^{\alpha}}^2}{\hbar^2} \right), \quad (31)$$

$$A_{22}^W(\vec{R}, \vec{P}) = \frac{|c_2|^2}{(\pi \hbar)^{3N}} \prod_{\alpha} \exp \left( \frac{-(R^{\alpha} - R_2^{\alpha})^2}{a_{R^{\alpha}}^2} \right) \times \exp \left( \frac{-(P^{\alpha} - P_2^{\alpha})^2 a_{R^{\alpha}}^2}{\hbar^2} \right), \quad (32)$$

$$\begin{aligned}
A_{12}^W(\vec{R}, \vec{P}) = & \frac{c_1 c_2^*}{(\pi \hbar)^{3N}} \prod_{\alpha} \exp\left(\frac{-(R^{\alpha} - \frac{1}{2}(R_1^{\alpha} + R_2^{\alpha}))^2}{a_{R^{\alpha}}^2}\right) \\
& \times \exp\left(\frac{-(P^{\alpha} - \frac{1}{2}(P_1^{\alpha} + P_2^{\alpha}))^2 a_{R^{\alpha}}^2}{\hbar^2}\right) \\
& \times \exp\left(\frac{i(R_2^{\alpha} - R_1^{\alpha})P^{\alpha}}{\hbar}\right) \exp\left(\frac{i(P_1^{\alpha} - P_2^{\alpha})R^{\alpha}}{\hbar}\right) \\
& \times \exp\left(\frac{i(P_2^{\alpha} - P_1^{\alpha})(R_2^{\alpha} + R_1^{\alpha})}{2\hbar}\right). \quad (33)
\end{aligned}$$

By integrating the squares of Eqs. (31) and (32) and plugging into Eq. (20), it is straightforward to prove (as it must be) that the impurity of a frozen Gaussian ansatz is always zero,  $S = 0$ .

Two key observations emerge from Eqs. (31)–(33):

1. According to exact quantum dynamics, the off-diagonal coherence matrix element  $A_{12}^W$  should pick up a phase that oscillates very quickly throughout phase space, proportional to  $(\vec{R}_1 - \vec{R}_2)$  and  $(\vec{P}_1 - \vec{P}_2)$ .
2. According to exact quantum dynamics, the off-diagonal coherence density in phase space is not centered at the same location as the on-diagonal population densities. In particular, the off-diagonal coherence density matrix is centered at  $(\vec{R}_1 + \vec{R}_2)/2, (\vec{P}_1 + \vec{P}_2)/2$ .

These two observations (nonlocal coherences and phase oscillations) explain the qualitative features we saw for exact quantum dynamics data in Figs. 3, 5, 8, and 11. The nonlocality of the  $A_{12}^W$  density in phase space is also completely consistent with the QCLE which postulates that, to first order in  $\hbar$ ,  $A_{12}^W$  coherences should be propagated with forces  $(\vec{F}_1 + \vec{F}_2)/2$  [while the populations  $A_{11}^W$  ( $A_{22}^W$ ) are propagated, of course, along  $\vec{F}_1$  ( $\vec{F}_2$ )].

As a sidenote, we mention that, even for a wavefunction with two frozen Gaussians on *the same* electronic surface  $A_{11}^W$  – the first wavepacket centered at  $(\vec{R}_1^{(a)}, \vec{P}_1^{(a)})$  and the second wavepacket centered at  $(\vec{R}_1^{(b)}, \vec{P}_1^{(b)})$  – one still finds a nonlocal peak in the Wigner transform centered at  $(\vec{R}_1^{(a)} + \vec{R}_1^{(b)})/2$  and  $(\vec{P}_1^{(a)} + \vec{P}_1^{(b)})/2$ . These nonlocal peaks are a well-known feature of Wigner transforms,<sup>57</sup> and this explains the peak in the middle of Fig. 11(a).

Overall, partially Wigner transformed density matrices can produce complicated, nonlocal phase space densities.

## B. FSSH predicts local coherences: An analytical measure of FSSH impurity

Let us now consider frozen Gaussian dynamics from the perspective of the FSSH and A-FSSH algorithms, and calculate our definition of impurity. To simplify the notation, we define  $f_1(\vec{R}, \vec{P})$  and  $f_2(\vec{R}, \vec{P})$  as the normalized nuclear den-

sities in phase space for adiabats 1 and 2 (for  $i = 1, 2$ ):

$$\begin{aligned}
f_i(\vec{R}, \vec{P}) = & \frac{1}{(\pi \hbar)^{3N}} \prod_{\alpha} \exp\left(\frac{-(R^{\alpha} - R_i^{\alpha})^2}{a_{R^{\alpha}}^2}\right) \\
& \times \exp\left(\frac{-(P^{\alpha} - P_i^{\alpha})^2 a_{R^{\alpha}}^2}{\hbar^2}\right). \quad (34)
\end{aligned}$$

For the FSSH algorithm, the diagonal elements of the partially Wigner transformed density matrix are then (for  $i = 1, 2$ )

$$A_{ii}(\vec{R}, \vec{P}) = |c_i|^2 f_i(\vec{R}, \vec{P}) \quad (35)$$

and it is easy to show that (for  $i = 1, 2$ )

$$\int_{-\infty}^{\infty} d\vec{R} \int_{-\infty}^{\infty} d\vec{P} f_i(\vec{R}, \vec{P}) = 1, \quad (36a)$$

$$\int_{-\infty}^{\infty} d\vec{R} \int_{-\infty}^{\infty} d\vec{P} f_i(\vec{R}, \vec{P})^2 = \frac{1}{(2\pi\hbar)^{3N}}. \quad (36b)$$

Hence, one can calculate that (for  $i = 1, 2$ )

$$\begin{aligned}
\int d\vec{R} \int d\vec{P} A_{ii}(\vec{R}, \vec{P})^2 = & \frac{1}{(2\pi\hbar)^{3N}} |c_i|^4 \\
= & \int_{-\infty}^{\infty} d\vec{R} \int_{-\infty}^{\infty} d\vec{P} A_{ii}^W(\vec{R}, \vec{P})^2. \quad (37)
\end{aligned}$$

In order to measure the impurity of a FSSH or A-FSSH calculation, we must also compute

$$\int d\vec{R} \int d\vec{P} |A_{12}(\vec{R}, \vec{P})|^2. \quad (38)$$

Now, as discussed in Ref. 32, there are several possible definitions for the off-diagonal matrix element within the FSSH algorithm and these definitions will not agree exactly using FSSH-like independent trajectories. Nevertheless, that being said, we will focus here on the definition in Eq. (19) for  $A_{12}$ , which we have found to be the most numerically stable formula available.<sup>32</sup> (For the other possible definitions of the off-diagonal matrix element discussed in Ref. 32, one must divide by a diagonal matrix element  $\sigma_{ii}$ ; thus, in cases where  $\sigma_{ii}$  gets small, one can potentially find a divergence of  $A_{12}$ .)

For a FSSH calculation with a frozen Gaussian ansatz, assuming each trajectory has consistent electronic amplitudes ( $c_1, c_2$ ), we will find (according to Eq. (19)) that

$$A_{12} = c_1 c_2^* (|c_1|^2 f_1 + |c_2|^2 f_2). \quad (39)$$

Notice that, according to Eq. (39),  $A_{12}$  has two peaks (one around the population on adiabat 1, one around the population on adiabat 2). This observation of two peaks agrees with our numerical results in Figs. 2, 4, 6, and 9, but this finding is in direct *disagreement* with the exact quantum answer. According to exact quantum dynamics, Eq. (33),  $A_{12}^W$  has only one peak centered in between the wavepackets on surfaces 1 and 2.

The disagreement between exact and FSSH-like methods for measuring coherences is a general failure of surface hopping: *Because the entire premise behind surface hopping is*

to build up both population and coherence phase space densities by following dynamics moving along adiabats, FSSH-like methods will never be able to fully capture nonlocal off-diagonal coherence densities centered far away from population densities.

Finally, to estimate the resulting FSSH impurity, we compute the integral of the square of the FSSH coherence as

$$\begin{aligned} & \int d\vec{R} \int d\vec{P} |A_{12}(\vec{R}, \vec{P})|^2 \\ &= \int d\vec{R} \int d\vec{P} |c_1|^2 |c_2|^2 (|c_1|^4 f_1^2 + |c_2|^4 f_2^2 + 2|c_1|^2 |c_2|^2 f_1 f_2) \\ &= \frac{|c_1|^2 |c_2|^2}{(2\pi\hbar)^{3N}} (|c_1|^4 + |c_2|^4) + 2|c_1|^4 |c_2|^4 \int d\vec{R} \int d\vec{P} f_1 f_2 \end{aligned} \quad (40)$$

which does not agree with

$$\int_{-\infty}^{\infty} d\vec{R} \int_{-\infty}^{\infty} d\vec{P} |A_{12}^W(\vec{R}, \vec{P})|^2 = \frac{1}{(2\pi\hbar)^{3N}} |c_1|^2 |c_2|^2. \quad (41)$$

If one assumes that the  $A_{11}$  and  $A_{22}$  densities are centered far away from each other and not overlapping, then the last term vanishes in Eq. (40). Substituting Eqs. (37) and (40) into Eq. (20), we find

$$\begin{aligned} S &= 1 - [ |c_1|^4 + |c_2|^4 + 2|c_1|^2 |c_2|^2 (|c_1|^4 + |c_2|^4) ] \\ &= 1 - (|c_1|^4 + |c_2|^4)(1 + 2|c_1|^2 |c_2|^2) \\ &= 1 - ((|c_1|^2 + |c_2|^2)^2 - 2|c_1|^2 |c_2|^2)(1 + 2|c_1|^2 |c_2|^2) \\ &= 1 - (1 - 2|c_1|^2 |c_2|^2)(1 + 2|c_1|^2 |c_2|^2) \\ &= 4|c_1|^4 |c_2|^4. \end{aligned} \quad (42)$$

Equation (42) gives us an analytical result for evaluating the total impurity of a surface-hopping calculation provided the wavefunction can be approximated as a sum of simple frozen Gaussians. The total impurity of a FSSH calculation becomes positive as soon as there is population on more than one adiabatic electronic surface.

In practice, to evaluate Eq. (42), the simplest approach is to calculate  $4|c_1|^4 |c_2|^4$  for each trajectory and then average the result over all FSSH trajectories. According to Fig. 13, we find that Eq. (42) does agree with the numerically calculated impurity for Tully #1 (which can indeed be viewed as a simple model problem with two frozen Gaussians). Tully #3 is a more complicated model Hamiltonian – with more than two frozen Gaussians – and Eq. (42) cannot be applied naively.

### C. The efficiency of FSSH comes at the expense of ignoring recoherences and not conserving impurity

Our discussion above of the frozen Gaussian model leads to a new understanding of the simultaneous limitations and strengths underlying all FSSH-like algorithms. On the one hand, these surface-hopping methods cannot treat correctly electronic coherences that are nonlocal in phase space and, therefore, these methods cannot correctly describe recoherences. Furthermore, the inability to capture recoherences

leads to an increasing value of total impurity for all FSSH-like calculations, whereas in truth total impurity must be conserved according to the exact dynamics of any closed system; impurity can grow only for an open quantum system. These are the failures of the surface hopping algorithm.

On the other hand, FSSH and A-FSSH are powerful tools for efficiently propagating nonadiabatic quantum dynamics in practice, and these methods can be derived approximately from the QCLE (assuming no recoherences). Furthermore, when measuring most expectation values, FSSH-like methods usually yield accurate observables because: (i) recoherences become increasingly uncommon for bigger and bigger systems at room temperature; (ii) when wavepackets are close together on different surfaces, surface hopping can capture the correct off-diagonal coherences; and (iii) when wavepackets move far apart on different surfaces, the correct off-diagonal matrix element picks up a rapidly oscillating phase that will integrate to zero in the stationary phase limit (Eq. (33)). Thus, even if FSSH-like methods cannot recover an electronic coherence that is stored nonlocally, for many expectation values, this failure will not be important. In practice, A-FSSH represents an improvement over FSSH dynamics by simply eliminating the spurious and incorrect FSSH coherences that arise when wavepackets bifurcate on different surfaces. In Figs. 14 and 15, we have shown that (unlike for FSSH) A-FSSH recovers the correct reduced electronic density matrix and electronic impurity (that grows in time).

The curious reader must surely ask him or herself whether another nonadiabatic dynamics algorithm exists that (i) offers the efficiency of the FSSH algorithm (which is easily simulated by standard Monte Carlo sampling) and also (ii) conserves the total impurity of the simulation exactly (by correctly describing all electronic coherences). Currently, many talented research groups are attacking this very problem in a myriad of different ways.<sup>58–64</sup> Only time will tell if such an optimal method arises—and if not, what is the optimal compromise we should make when choosing an approximate nonadiabatic dynamics method?

## VI. CONCLUSIONS

In this paper, we have given a simple prescription (based on purity) for evaluating the total impurity of a system described by a partially Wigner transformed density matrix. We demonstrated that, according to our definition, exact quantum dynamics and the QCLE conserve the total impurity of a closed system in time, but that FSSH and FSSH-like methods do not conserve total impurity. (For simple cases, we derived an analytic expression for the total impurity.) We attributed this failure of surface-hopping methods to the inability of FSSH-like methods to recover the correct, nonlocal off-diagonal density matrix in phase space (or capture wavepacket recoherences). We noted, however, that in the limit of large separations between wavepackets on different surfaces, electronic coherences oscillate very quickly in phase space and should not contribute meaningfully to expectation values. Thus, we have argued that surface-hopping dynamics can make accurate predictions of observables in spite of the method's failure to conserve the total impurity of a closed

system. Moreover, for the electronic subsystem, A-FSSH is able to deliver a reasonably accurate reduced density matrix and a very accurate electronic impurity (that grows in time correctly). Future work in nonadiabatic dynamics will no doubt explore how important total impurity conservation is when studying large (but closed) quantum systems designed to represent the condensed phase. After all, usually in chemistry we are interested in the impurity and dynamics of subsystems.

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