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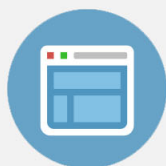
Can we derive Tully's surface-hopping algorithm from the semiclassical quantum Liouville equation? Almost, but only with decoherence

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In this article, we demonstrate that Tully's fewest-switches surface hopping (FSSH) algorithm approximately obeys the mixed quantum-classical Liouville equation (QCLE), provided that several conditions are satisfied – some major conditions, and some minor. The major conditions are: (1) nuclei must be moving quickly with large momenta; (2) there cannot be explicit recoherences or interference effects between nuclear wave packets; (3) force-based decoherence must be added to the FSSH algorithm, and the trajectories can no longer rigorously be independent (though approximations for independent trajectories are possible). We furthermore expect that FSSH (with decoherence) will be most robust when nonadiabatic transitions in an adiabatic basis are dictated primarily by derivative couplings that are presumably localized to crossing regions, rather than by small but pervasive off-diagonal force matrix elements. In the end, our results emphasize the strengths of and possibilities for the FSSH algorithm when decoherence is included, while also demonstrating the limitations of the FSSH algorithm and its inherent inability to follow the QCLE exactly. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4829856]

I. INTRODUCTION: AN *AD HOC* SURFACE HOPPING VIEW OF NONADIABATIC DYNAMICS

John Tully's fewest-switches surface-hopping (FSSH) algorithm[1] is perhaps the most popular method for calculating nonadiabatic transition rates, whereby electrons can relax in exchange for an increase in nuclear kinetic energy. Thus far, however, Tully's algorithm has never been derived from the Schrödinger equation. In this sense, FSSH is very different from the Miller-Meyer-Stock-Thoss formalism (MMST)[2–5] or *ab initio* multiple spawning.[6,7] For many practicing theorists, the FSSH algorithm has been justified mostly from empirical experience: the approach is simple, capturing the intuitive physics of many problems, and very often happens to give reasonable rates of electronic relaxation.

Of course, the FSSH algorithm does suffer from a few well-known drawbacks, and there have been numerous attempts to improve the algorithm. In particular, the largest failure of FSSH is its inability to treat decoherence, i.e., the bifurcation of nuclear wave packets moving on different electronic surfaces.[1,8] The decoherence problem in surface-hopping arises because all FSSH nuclear trajectories carry along their own personal electronic density matrix to simulate a coherent wave packet on different surfaces, but the electronic density matrix is never updated when trajectories move apart. One signature of the decoherence problem is that one finds artificial oscillations or specious resonances in long time dynamics, and this leads to the wrong scaling law[9] for the Marcus problem[10,11] in the nonadiabatic limit (among other failures). Over the past 15 years, beginning in earnest with the work of Rossky, Prezhdo and Schwartz,[12,13] there has been a great deal of research devoted to improving FSSH to allow for decoherence. The general scheme is to collapse the electronic amplitudes to simulate wave packet separation, and important contributions have been made by several authors.[14–25] A nice summary of the different schemes is given in Ref. 26. Including decoherence on top of the FSSH algorithm does restore the correct scaling for the Marcus problem.[9,27]

As a practical matter, if we want to fix up Tully's FSSH algorithm, our immediate question is usually: what is the correct rate of that decoherence? But another inevitable question is: can one really improve FSSH dynamics given that the FSSH scheme itself cannot be truly derived? Is this a well-defined scientific goal? Or perhaps we should go all the way back to the Schrödinger equation?[28–30]

The analytical theory closest to FSSH dynamics is the mixed quantum-classical Liouville equation (QCLE) approach studied by Martens,[31,32] Kapral,[33,34] and others.[35–41] The general idea is to perform a partial Wigner transform and then monitor the time evolution of the joint nuclear-electronic probability density in classical phase space using a truncated equation of motion. Kapral[42–44] has shown that one can generate trajectories to simulate such phase space distributions, but the resulting averages are not always stable (though filtering helps). Kapral's[33,34] momentum-jump trajectories have some elements in common[8] with John Tully's FSSH algorithm, but they are different in spirit as well as in substance. In particular, Kapral's[33,34] momentum-jump trajectories can follow not just one adiabatic surface potential but also sometimes the mean of the two different adiabatic potentials (which is very different from FSSH). A concise and clear summary of the method is given in Ref. 45.

With this background, the goal of the present paper is to connect John Tully's FSSH algorithm with the Martens/Kapral quantum-classical Liouville equation. We will show that, under certain conditions – some of which we

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TABLE I. List of the assumptions required (major and minor) to connect FSSH to the QCLE, and the corresponding equations where these assumptions are discussed or applied.

	Applicable equations
Major conditions	
#1 Unique trajectory assumption	(28)
#2 Large velocity assumption	(29)
#3 Modified electronic density matrix propagation	
(option #a: fully general implementation is stable)	(51)–(57), (66)
(option #b: single term correction is stable and accurate)	(58), (59), (68)
(option #c: fully general implementation (restricted to $\gamma > 0$) is accurate)	(51)–(57), (66)
(option #d: single term correction (restricted to $\gamma > 0$) is accurate)	(58), (59), (68)
Minor conditions	
Positivity of partial Wigner density matrix at time $t = 0$	(21), (22)
Separability of electronic and nuclear density matrices at time $t = 0$	(22)
Dominance of the derivative coupling term in establishing sign of hopping rate	(33)–(35)
Heaviside hopping rate replaced by 1/2 times rate	(3), (48)

consider major, some of which we consider minor – John Tully's algorithm does satisfy the quantum-classical Liouville equation, *provided that decoherence is treated properly*. For completeness, in Table I we list all the assumptions (major and minor) required to connect FSSH to the QCLE. Until there is more empirical data available, we will leave it to the reader to decide for him or herself the limitations of these assumptions.

Henceforward, we will work exclusively here with the case of two adiabatic states, 1 and 2. Extensions to more than two electronic surfaces should be straightforward.

Notation: A word about notation is in order. Below, i, j, k will reference electronic states; λ will represent the active adiabatic surface which is being followed by a nuclear trajectory. For the most part, we will treat two electronic states, 1 and 2. Nuclear coordinates will be labeled α, β. Unless stated otherwise, whenever α or β appears more than once in an equation, a summation over all nuclear coordinates is implied. We will denote σ as an electronic density matrix, while $\mathbf{A}$ will represent a full or nuclear-electronic density matrix.

II. THEORY: QCLE AND FSSH IN DETAIL

We now give very brief overviews of the QCLE and the FSSH algorithm, before connecting the two.

A. Quantum-classical Liouville equation

In discussing the quantum-classical Liouville equation, we will follow Kapral's approach.[33,34] Accordingly, one first carries out a partial Wigner transform over only the classical degrees of freedom

$$A_{ij}^W(\vec{R}, \vec{P}, t)$$

$$\equiv \left(\frac{1}{2\pi\hbar}\right)^{3N} \int d\vec{X} e^{i\vec{P}\cdot\vec{X}/\hbar} \left\langle \Phi_i(\vec{R}); \vec{R} - \frac{\vec{X}}{2} \middle| \Psi(t) \right\rangle$$

$$\times \left\langle \Psi(t) \middle| \Phi_j(\vec{R}); \vec{R} + \frac{\vec{X}}{2} \right\rangle, \tag{1}$$

where nuclear coordinate space is $3N$ dimensional and $\vec{X}$ serves as a dummy variable. $|\Psi(t)\rangle$ is the full nuclear-electronic wavefunction at time t. The electronic wavefunctions $|\Phi_i(\vec{R})\rangle$ and $|\Phi_j(\vec{R})\rangle$ are chosen here as the (adiabatic) eigenfunctions of the electronic Hamiltonian at position $\vec{R}$.

Second, as we evolve in time, the equation of motion for the partial Wigner transform in an adiabatic basis is (to first order in the electron-nucleus mass ratio $(m/M)^{1/2}$)[33]

$$\frac{\partial}{\partial t} A_{ij}^W(\vec{R}, \vec{P}, t)$$

$$= \frac{-i}{\hbar}(V_{ii}(\vec{R}) - V_{jj}(\vec{R}))A_{ij}^W$$

$$- \frac{P^\alpha}{M^\alpha} \sum_k \left(d_{ik}^\alpha(\vec{R})A_{kj}^W - A_{ik}^W d_{kj}^\alpha(\vec{R})\right) - \frac{P^\alpha}{M^\alpha} \frac{\partial A_{ij}^W}{\partial R^\alpha}$$

$$- \frac{1}{2} \sum_k \left(F_{ik}^\alpha(\vec{R})\frac{\partial A_{kj}^W}{\partial P^\alpha} + \frac{\partial A_{ik}^W}{\partial P^\alpha} F_{kj}^\alpha(\vec{R})\right). \tag{2}$$

Here, $V_{ii}(\vec{R})$ are the adiabatic potential energy surfaces and $\{F_{ij}(\vec{R})\}$ are the set of forces, $F_{ij}^\alpha(\vec{R}) \equiv -\langle \Phi_i(\vec{R})|\frac{\partial V}{\partial R^\alpha}|\Phi_j(\vec{R})\rangle$. $d_{ij}^\alpha(\vec{R})$ are the derivative couplings, $d_{ij}^\alpha(\vec{R}) \equiv F_{ij}^\alpha(\vec{R})/(V_{ii}(\vec{R}) - V_{jj}(\vec{R}))$ with $i \neq j$.

For convenience later, let us write out the diagonal and off-diagonal equations in Eq. (2) separately, assuming an adiabatic basis with only two electronic states, 1 and 2

$$\frac{\partial}{\partial t} A_{11}^W(\vec{R}, \vec{P}, t) = -\frac{P^\alpha}{M^\alpha}(d_{12}^\alpha A_{21}^W - A_{12}^W d_{21}^\alpha) - \frac{P^\alpha}{M^\alpha}\frac{\partial A_{11}^W}{\partial R^\alpha}$$

$$- F_{11}^\alpha \frac{\partial A_{11}^W}{\partial P^\alpha} - \frac{1}{2}\left(F_{12}^\alpha \frac{\partial A_{21}^W}{\partial P^\alpha} + \frac{\partial A_{12}^W}{\partial P^\alpha} F_{21}^\alpha\right) \tag{3}$$

and

$$\frac{\partial}{\partial t} A_{12}^W(\vec{R}, \vec{P}, t) = \frac{-i}{\hbar}(V_{11} - V_{22})A_{12}^W$$
$$- \frac{P^\alpha}{M^\alpha} d_{12}^\alpha (A_{22}^W - A_{11}^W) - \frac{P^\alpha}{M^\alpha}\frac{\partial A_{12}^W}{\partial R^\alpha}$$
$$- \frac{1}{2}(F_{11}^\alpha + F_{22}^\alpha)\frac{\partial A_{12}^W}{\partial P^\alpha}$$
$$- \frac{1}{2}F_{12}^\alpha\left(\frac{\partial A_{11}^W}{\partial P^\alpha} + \frac{\partial A_{22}^W}{\partial P^\alpha}\right). \quad (4)$$

To simplify our notation, we will not always include the dependence of $\vec{F}$, $\vec{V}$, and $\vec{d}_{12}$ on position $\vec{R}$, i.e., $\vec{F} \equiv \vec{F}(\vec{R})$

B. Tully's FSSH algorithm

We would like to connect the Tully ansatz with the mixed quantum-classical Liouville approach above. To that end, one can ask: what equation of motion does surface hopping satisfy in mixed quantum-classical phase space? We will answer this question in Sec. III. For now, let us review FSSH dynamics[1] and establish our notation. In brief, FSSH dynamics includes three main ingredients.

1. Classical movement along the adiabatic surfaces

We start with a swarm of trajectories, each with its own electronic amplitudes **c** or electronic density matrix $\boldsymbol{\sigma}$. For our purposes, it will be helpful to label these electronic quantities by the surfaces along which the nuclei move; hence, we will use the notations $\mathbf{c}^{(\lambda)}$ and $\boldsymbol{\sigma}^{(\lambda)}$ to indicate that the corresponding nuclear trajectory follows surface $\lambda = 1, 2$. λ is sometimes called the *active* surface or state. For a particle moving along surface λ, the electronic density matrix is

$$\boldsymbol{\sigma}^{(\lambda)} \equiv \begin{pmatrix} \sigma_{11}^{(\lambda)} & \sigma_{12}^{(\lambda)} \\ \sigma_{21}^{(\lambda)} & \sigma_{22}^{(\lambda)} \end{pmatrix} \equiv \begin{pmatrix} c_1^{(\lambda)}c_1^{(\lambda)*} & c_1^{(\lambda)}c_2^{(\lambda)*} \\ c_2^{(\lambda)}c_1^{(\lambda)*} & c_2^{(\lambda)}c_2^{(\lambda)*} \end{pmatrix}. \quad (5)$$

All nuclei move classically along a single adiabatic potential energy surface (λ)

$$\frac{dR^\alpha}{dt} = \frac{P^\alpha}{M^\alpha}, \quad (6)$$

$$\frac{dP^\alpha}{dt} = F_{\lambda\lambda}^\alpha. \quad (7)$$

(Clearly, no summation over α is implied in Eq. (6).) Independent of the active surface (λ), the electronic amplitudes ($c_1^{(\lambda)}, c_2^{(\lambda)}$) obey the electronic time-dependent electronic Schrödinger equation (where the nuclear position $\vec{R}$ and momentum $\vec{P}$ are just parameters),

$$\frac{dc_n^{(\lambda)}}{dt} = -\frac{i}{\hbar}\sum_k V_{nk}(\vec{R})c_k^{(\lambda)} - \sum_k \frac{P^\alpha}{M^\alpha}d_{nk}^\alpha(\vec{R})c_k^{(\lambda)}. \quad (8)$$

The corresponding electronic density matrix $\boldsymbol{\sigma}^{(\lambda)}$ satisfies an effective Liouville equation

$$\frac{d}{dt}\sigma_{nk}^{(\lambda)}(t) = -\frac{i}{\hbar}[\mathbf{V}, \boldsymbol{\sigma}^{(\lambda)}]_{nk} - \frac{P^\alpha}{M^\alpha}[\mathbf{d}^\alpha, \boldsymbol{\sigma}^{(\lambda)}]_{nk}. \quad (9)$$

As we did above in Eqs. (3) and (4), it will be helpful to write out Eq. (9) for the diagonal and off-diagonal components separately, assuming only two electronic states

$$\frac{d}{dt}\sigma_{11}^{(\lambda)}(t) = -\frac{P^\alpha}{M^\alpha}\left(d_{12}^\alpha\sigma_{21}^{(\lambda)} - \sigma_{12}^{(\lambda)}d_{21}^\alpha\right), \quad (10)$$

$$\frac{d}{dt}\sigma_{12}^{(\lambda)}(t) = -\frac{i}{\hbar}(V_{11} - V_{22})\sigma_{12}^{(\lambda)} - \frac{P^\alpha}{M^\alpha}d_{12}^\alpha\left(\sigma_{22}^{(\lambda)} - \sigma_{11}^{(\lambda)}\right). \quad (11)$$

2. Momentum rescaling

For most FSSH applications, we assume that (at time 0), all particles start on a single adiabatic surface, which makes trajectory initialization straightforward. As time proceeds, electronic relaxation is accomplished by stochastic hops between active surfaces. Each hop is accompanied by a momentum rescaling in the direction of the derivative coupling to maintain energy conservation.

Let us suppose that $\lambda = 1$ is the active surface. For a hop from $\lambda = 1$ to $\lambda = 2$, the change in momentum can always be written $\Delta\vec{P} = \Delta P \hat{d}_{12}$, where $\hat{d}_{12}$ is a unit vector in the direction of the derivative couplings, $\hat{d}_{12} = \vec{d}_{12}/|\vec{d}_{12}|$. Energy conservation implies

$$\frac{(P^\alpha + \Delta P \hat{d}_{12}^\alpha)^2}{2M^\alpha} + \Delta E = \frac{(P^\alpha)^2}{2M^\alpha}, \quad (12)$$

$$\Rightarrow \Delta P \approx -\frac{\Delta E}{\frac{P^\alpha \hat{d}_{12}}{M^\alpha}} + O(\Delta P^2), \quad (13)$$

$$\Delta E = V_2 - V_1. \quad (14)$$

If an upward hop is attempted but the trajectory does not have enough kinetic energy to maintain energy conservation, then the hop is rejected. The role of such *forbidden hops* will not be addressed in this paper – we will find below that FSSH corresponds to the QCLE in the case that nuclei carry large momenta.

3. Hopping rate, consistency, and decoherence

According to its very name, the FSSH algorithm proposes that hops between adiabatic surfaces should occur as the minimal rate so as to accomplish electronic relaxation. To be precise, suppose that at time t we have N_1 trajectories at $(\vec{R}, \vec{P})$ in phase space on surface 1 and N_2 trajectories on surface 2. One can estimate the overall relaxation of particles from surface $1 \rightarrow 2$ in time dt by considering the time-dependent electronic Schrödinger equation (Eq. (10))[1] and one concludes

$$\gamma_{tot}^{1\rightarrow 2} = \frac{2P^\alpha}{M^\alpha}\text{Re}\left(d_{12}^\alpha(\vec{R})\sigma_{21}^{(1)}\right)dt. \quad (15)$$

To achieve this overall rate of electronic relaxation, one could allow both surface excitations and de-excitations provided that

$$N_1\gamma_{hop}^{1\rightarrow 2} - N_2\gamma_{hop}^{2\rightarrow 1} = N_{tot}\gamma_{tot}^{1\rightarrow 2}. \quad (16)$$

Tully's FSSH algorithm proposes, however, that there should not be any unnecessary jumps. Let us suppose that, without

loss of generality, there is a positive overall rate of transfer from surface 1 to 2. In this case, one sets $\gamma_{hop}^{2\to1} = 0$, so that

$$\gamma_{hop}^{1\to2} = \gamma_{tot}^{1\to2} \frac{N_{tot}}{N_1}. \qquad (17)$$

Finally, Tully[1] assumes self-consistency of the amplitudes and trajectories. Mathematically, Tully[1] assumes that

$$\frac{N_1}{N_{tot}} = \sigma_{11}^{(1)} \qquad (18)$$

resulting in the final hopping rate for FSSH

$$\gamma_{hop}^{1\to2} = \Gamma\left[\frac{2P^\alpha}{M^\alpha} \frac{\text{Re}\left(d_{12}^\alpha(\vec{R})\sigma_{21}^{(1)}\right)}{\sigma_{11}^{(1)}} dt \right]. \qquad (19)$$

Here, Γ represents the positive projector

$$\Gamma[x] = \Theta[x] \cdot x = \begin{cases} x & x \geq 0 \\ 0 & x < 0 \end{cases}, \qquad (20)$$

where Θ is a Heaviside function.

Two important comments are in order regarding Eqs. (18) and (19). First, according to Eq. (19), the hopping rate from surface 1 to 2 depends only on the local dynamics on surface 1. This feature allows one to implement FSSH easily via independent trajectories. Second, the self-consistency assumed in Eq. (18) is not true in general and can be violated badly. Beyond forbidden hops,[46] this lack of self-consistency can be explained very easily by the fact that particles moving along different surfaces feel different forces, which leads to a bifurcation of wave packets on different surfaces. However, because the electronic density matrix of each FSSH trajectory has infinite memory, FSSH wave packets are never really able to separate,[47,48] and the resulting lack of self-consistency eventually leads to incorrect "overly coherent" dynamics.[14,49] Thus, Eq. (18) will not hold in general, especially when different adiabatic surfaces have very different forces.

In summary, Tully's FSSH algorithm constitutes three core components: classical movement along adiabatic surfaces, the specific hopping rate in Eq. (19), and post-hop momentum rescaling according to Eq. (12). When FSSH algorithm fails to provide accurate results, one common culprit is the decoherence problem, which is manifested in the failure of Eq. (18) to hold (i.e., the lack of self-consistency). Over the years many modifications of FSSH have been proposed to include decoherence.[12–25] Notably, when we provide a rough but almost rigorous derivation of Tully's algorithm, the reader will find below in Sec. III C that the decoherence problem resurfaces (as it must).

III. THEORY: A NUCLEAR-ELECTRONIC DENSITY MATRIX FOR FSSH

To connect FSSH trajectories with the QCLE, we will need to build a nuclear-electronic density matrix for FSSH.

A. On-diagonal full density matrix elements

For FSSH dynamics, the natural on-diagonal full density matrix should depend only on the active surfaces (λ) of nuclear propagation, rather than electronic amplitudes $\mathbf{c}$

or electronic density matrix $\boldsymbol{\sigma}$. The reasoning is very simple: Schmidt, Parandekar, and Tully[50,51] have shown that, in equilibrium, the active adiabatic surface populations approximately obey detailed balance while the amplitudes become meaningless at long times, usually approaching infinite temperature. With this in mind, we define the on-diagonal full density matrix for FSSH as

$$A_{11}(\vec{R}, \vec{P}, t) \equiv \lim_{N_{traj}\to\infty} \frac{1}{N_{traj}} \sum_{traj} \sum_{\lambda_0} \int d\vec{R}_0 \int d\vec{P}_0$$
$$\times A_{\lambda_0\lambda_0}^W(\vec{R}_0, \vec{P}_0)\delta(\vec{R}(t; \vec{R}_0, \vec{P}_0, \lambda_0) - \vec{R})$$
$$\times \delta(\vec{P}(t; \vec{R}_0, \vec{P}_0, \lambda_0) - \vec{P})\delta_{\lambda(t),1}. \qquad (21)$$

Several points must now be made about this definition.

- In Eq. (21), we sum over all FSSH trajectories starting in phase space at $(\vec{R}_0, \vec{P}_0)$ at time 0, and moving along surface λ_0 initially. The sum/integral are nonzero only for those trajectories that reach $(\vec{R}, \vec{P})$ at time t with surface 1 active.

- The sum over trajectories (and division by N_{traj}) is necessary because FSSH trajectories are stochastic; each trajectory in effect corresponds to a unique time-dependent random number generator.

- By choosing our sampling function in Eq. (21) as the partial Wigner phase space $A^W(\vec{R}_0, \vec{P}_0)$ distribution (i.e., Eq. (1)), we ensure that $A_{11}(\vec{R}_0, \vec{P}_0) = A_{11}^W(\vec{R}_0, \vec{P}_0)$ at $t = 0$.

- Technically, the definition in Eq. (21) is incomplete because a complete FSSH trajectory also includes the electronic density matrix, $\boldsymbol{\sigma}_0^{(\lambda_0)}(\vec{R}_0, \vec{P}_0)$. Thus, to be completely rigorous, we should write, e.g., $\vec{R}(t; \vec{R}_0, \vec{P}_0, \lambda_0, \boldsymbol{\sigma}_0)$ instead of just $\vec{R}(t; \vec{R}_0, \vec{P}_0, \lambda_0)$. To that end, we will define the initial electronic density matrix as

$$\boldsymbol{\sigma}_0^{(1)}(\vec{R}_0, \vec{P}_0) \equiv \boldsymbol{\sigma}_0^{(2)}(\vec{R}_0, \vec{P}_0)$$
$$\equiv \frac{\mathbf{A}^W(\vec{R}_0, \vec{P}_0, 0)}{A_{11}^W(\vec{R}_0, \vec{P}_0, 0) + A_{22}^W(\vec{R}_0, \vec{P}_0, 0)}. \qquad (22)$$

(Note that Eq. (22) is compatible with Eqs. (31) and (32) below.) It can be easily proved that $\boldsymbol{\sigma}_0(\vec{R}_0, \vec{P}_0)$ in Eq. (22) represents a pure state (with $\sigma_{11}\sigma_{22} - \sigma_{12}\sigma_{21} = 0$ as required by FSSH) only when the electronic state and nuclear wave packet are exactly factorizable, i.e., $\boldsymbol{\rho}_{total}(t = 0) = \boldsymbol{\rho}_{elec} \otimes \boldsymbol{\rho}_{nuc}$. In other words, FSSH dynamics should be initialized at $t = 0$ only when there is no electronic-nuclear entanglement (so $\boldsymbol{\sigma}_0^{(1)}(\vec{R}_0, \vec{P}_0) = \boldsymbol{\sigma}_0^{(2)}(\vec{R}_0, \vec{P}_0) = \boldsymbol{\sigma}_0$), e.g., after a Franck-Condon excitation to an excited state. This is the usual case for which FSSH dynamics is applied – and this holds for many other nonadiabatic theories as well, e.g., Redfield theory. Admittedly, this restriction could be a limitation for some applications.

- From Eq. (22), we must assume here that the $A_{11}^W(\vec{R}_0, \vec{P}_0)$ and $A_{22}^W(\vec{R}_0, \vec{P}_0)$ distributions are positive at time 0, which need not be true. Nevertheless, in practice, FSSH trajectories are almost always initialized from a classical (and hence, clearly, positive)

distribution, and we do not believe this assumption represents a practical limitation of the method. We will classify this as a minor condition in Table I.

- In Eq. (21), $\delta(\vec{P}(t; \vec{R}_0, \vec{P}_0, \lambda_0) - \vec{P})$ is a Dirac delta function, while $\delta_{\lambda(t), 1}$ is a Kronecker delta function.

1. Major condition #1: Unique trajectory assumption

At this point, we have presumed that FSSH dynamics are initialized only when there is a unique electronic density matrix $\boldsymbol{\sigma}_0$ for each point in phase space at time $t = 0$. Of course,

as time advances, trajectories on different surfaces will move differently and pick up different electronic amplitudes. We can now stipulate condition #1 for FSSH to agree with QCLE for times $t \geq 0$: for each point in phase space $(\vec{R}, \vec{P})$ and each electronic surface (λ), there should correspond exactly one unique trajectory with electronic density matrix $\sigma_{ij}^{(\lambda)}(\vec{R}, \vec{P}, t)$. This must be true for short times, but it also highlights that surface-hopping cannot recover recoherences at a fundamental level.

Using this assumption, if we take the partial derivative of $A_{11}(\vec{R}, \vec{P}, t)$, we find

$$\frac{\partial A_{11}(\vec{R}, \vec{P}, t)}{\partial t} = \lim_{N_{traj} \to \infty} \frac{1}{N_{traj}} \sum_{traj} \sum_{\lambda_0} \int d\vec{R}_0 \int d\vec{P}_0 \, A_{\lambda_0 \lambda_0}^W (\vec{R}_0, \vec{P}_0)$$

$$\times \left\{ \frac{\partial \delta(\vec{R}(t; \vec{R}_0, \vec{P}_0, \lambda_0) - \vec{R})}{\partial t} \delta(\vec{P}(t; \vec{R}_0, \vec{P}_0, \lambda_0) - \vec{P}) \delta_{\lambda(t), 1} \right.$$

$$+ \delta(\vec{R}(t; \vec{R}_0, \vec{P}_0, \lambda_0) - \vec{R}) \frac{\partial \delta(\vec{P}(t; \vec{R}_0, \vec{P}_0, \lambda_0) - \vec{P})}{\partial t} \delta_{\lambda(t), 1}$$

$$\left. + \delta(\vec{R}(t; \vec{R}_0, \vec{P}_0, \lambda_0) - \vec{R}) \delta(\vec{P}(t; \vec{R}_0, \vec{P}_0, \lambda_0) - \vec{P}) \frac{\partial \delta_{\lambda(t), 1}}{\partial t} \right\}. \tag{23}$$

To simplify Eq. (23), note that (with shorthand $\vec{R}_t = \vec{R}(t; \vec{R}_0, \vec{P}_0, \lambda_0)$)

$$\frac{\partial \delta(\vec{R}_t - \vec{R})}{\partial t} = \frac{\partial \delta(\vec{R}_t - \vec{R})}{\partial R_t^\alpha} \frac{\partial R_t^\alpha}{\partial t} = -\frac{\partial \delta(\vec{R}_t - \vec{R})}{\partial R^\alpha} \frac{P_t^\alpha}{M^\alpha} \tag{24}$$

and similarly for the $\frac{\partial}{\partial P^\alpha}$ term. Pulling the $\frac{\partial}{\partial R^\alpha}$ and $\frac{\partial}{\partial P^\alpha}$ derivatives out of the integral, we find

$$\frac{\partial A_{11}(\vec{R}, \vec{P}, t)}{\partial t} = -\frac{\partial A_{11}(\vec{R}, \vec{P}, t)}{\partial R^\alpha} \frac{P^\alpha}{M^\alpha} - \frac{\partial A_{11}(\vec{R}, \vec{P}, t)}{\partial P^\alpha} F_{11}^\alpha$$

$$+ \lim_{N_{traj} \to \infty} \frac{1}{N_{traj}} \sum_{traj} \sum_{\lambda_0} \int d\vec{R}_0 \int d\vec{P}_0 \, A_{\lambda_0 \lambda_0}^W (\vec{R}_0, \vec{P}_0) \, \delta(\vec{R}_t - \vec{R}) \delta(\vec{P}_t - \vec{P}) \frac{\partial \delta_{\lambda(t), 1}}{\partial t}. \tag{25}$$

Next, the last term in Eq. (25) (with $\frac{\partial \delta_{\lambda(t), 1}}{\partial t}$) represents hopping between surfaces with a continuous probability. As with any master equation, the time rate of change is just the gain (hops from surface 2 to surface 1) minus the loss (hops from surface 1 to surface 2). Thus,

$$\frac{\partial A_{11}(\vec{R}, \vec{P}, t)}{\partial t} = -\frac{\partial A_{11}(\vec{R}, \vec{P}, t)}{\partial R^\alpha} \frac{P^\alpha}{M^\alpha} - \frac{\partial A_{11}(\vec{R}, \vec{P}, t)}{\partial P^\alpha} F_{11}^\alpha \tag{26}$$

$$+ A_{22}(\vec{R}, \vec{P} + \Delta \vec{P}, t) \gamma_{hop}^{2 \to 1} - A_{11}(\vec{R}, \vec{P}, t) \gamma_{hop}^{1 \to 2}. \tag{27}$$

At this point, we invoke Eq. (19), i.e., the hopping rate according to FSSH, yielding

$$\frac{\partial A_{11}(\vec{R}, \vec{P}, t)}{\partial t} = -\frac{\partial A_{11}(\vec{R}, \vec{P}, t)}{\partial R^\alpha} \frac{P^\alpha}{M^\alpha} - \frac{\partial A_{11}(\vec{R}, \vec{P}, t)}{\partial P^\alpha} F_{11}^\alpha - \Gamma \left[\left(d_{12}^\alpha \sigma_{21}^{(1)} - \sigma_{12}^{(1)} d_{21}^\alpha \right) \frac{P^\alpha}{M^\alpha} \frac{1}{\sigma_{11}^{(1)}} A_{11}(\vec{R}, \vec{P}, t) \right]$$

$$+ \Gamma \left[\left(d_{21}^\alpha \sigma_{12}^{(2)}(\vec{P} + \Delta P \hat{d}_{12}) - \sigma_{21}^{(2)}(\vec{P} + \Delta P \hat{d}_{12}) d_{12}^\alpha \right) \frac{(P^\alpha + \Delta P \hat{d}_{12}^\alpha)}{M^\alpha} \frac{1}{\sigma_{22}^{(2)}(\vec{P} + \Delta P \hat{d}_{12})} A_{22}(\vec{R}, \vec{P} + \Delta P \hat{d}_{12}, t) \right], \tag{28}$$

where $\boldsymbol{\sigma}^{(1)}$ and $\boldsymbol{\sigma}^{(2)}$ are the unique (by assumption) electronic density matrices found on surfaces 1 and 2, respectively.

2. Major condition #2: Large velocity assumption

We now assert condition #2 that is required for FSSH and QCLE agreement: the large momentum assumption. In this case, $|\Delta P| \ll |\vec{P} \cdot \hat{d}_{12}|$ and we can expand all quantities in Eq. (28) as a Taylor series in ΔP. All phase space densities are now evaluated at $(\vec{R}, \vec{P}, t)$

$$\frac{\partial A_{11}(\vec{R}, \vec{P}, t)}{\partial t} = -\frac{\partial A_{11}}{\partial R^\alpha} \frac{P^\alpha}{M^\alpha} - \frac{\partial A_{11}}{\partial P^\alpha} F_{11}^\alpha$$

$$-\Gamma \left[\left(d_{12}^\alpha \sigma_{21}^{(1)} - \sigma_{12}^{(1)} d_{21}^\alpha\right) \frac{P^\alpha}{\sigma_{11}^{(1)} M^\alpha} A_{11} \right]$$

$$+\Gamma \left[\begin{array}{c} \left(d_{21}^\alpha \sigma_{12}^{(2)} - \sigma_{21}^{(2)} d_{12}^\alpha\right) \dfrac{P^\alpha}{\sigma_{22}^{(2)} M^\alpha} A_{22} \\[2mm] + \left(d_{21}^\alpha \sigma_{12}^{(2)} - \sigma_{21}^{(2)} d_{12}^\alpha\right) \dfrac{P^\alpha \Delta P \hat{d}_{12}^\beta}{\sigma_{22}^{(2)} M^\alpha} \dfrac{\partial A_{22}}{\partial P^\beta} \\[2mm] + \left(d_{21}^\alpha \dfrac{\partial \sigma_{12}^{(2)}}{\partial P^\beta} - \dfrac{\partial \sigma_{21}^{(2)}}{\partial P^\beta} d_{12}^\alpha\right) \dfrac{P^\alpha \Delta P \hat{d}_{12}^\beta}{\sigma_{22}^{(2)} M^\alpha} A_{22} \\[2mm] - \left(d_{21}^\alpha \sigma_{12}^{(2)} - \sigma_{21}^{(2)} d_{12}^\alpha\right) \dfrac{P^\alpha \Delta P \hat{d}_{12}^\beta}{\left(\sigma_{22}^{(2)}\right)^2 M^\alpha} \dfrac{\partial \sigma_{22}^{(2)}}{\partial P^\beta} A_{22} \\[2mm] + \left(d_{21}^\alpha \sigma_{12}^{(2)} - \sigma_{21}^{(2)} d_{12}^\alpha\right) \dfrac{\Delta P \hat{d}_{12}^\alpha}{\sigma_{22}^{(2)} M^\alpha} A_{22} \end{array} \right] + O(\Delta P^2). \qquad (29)$$

By virtue of the large momentum assumption, we can ignore the term $\left(d_{21}^\alpha \sigma_{12}^{(2)} - \sigma_{21}^{(2)} d_{12}^\alpha\right) \frac{\Delta P \hat{d}_{12}^\alpha}{\sigma_{22}^{(2)} M^\alpha} A_{22}$ in the second Γ argument in Eq. (29). For the reader familiar with QCLE dynamics, note that disregard of the $O(\Delta P^2)$ terms in Eq. (29) is effectively equivalent to the Kapral-Ciccotti momentum-jump approximation.[33]

At this point, we plug in for ΔP. Because $\Delta P \frac{P^\alpha d_{12}^\alpha}{M^\alpha} \approx -\Delta E |\vec{d}_{12}|$ and $d_{12}^\alpha \Delta E = -F_{12}^\alpha$, the terms above simplify and we can write

$$\frac{\partial A_{11}(\vec{R}, \vec{P}, t)}{\partial t} \approx -\frac{\partial A_{11}}{\partial R^\alpha} \frac{P^\alpha}{M^\alpha} - \frac{\partial A_{11}}{\partial P^\alpha} F_{11}^\alpha - \Gamma \left[\left(d_{12}^\alpha \sigma_{21}^{(1)} - \sigma_{12}^{(1)} d_{21}^\alpha\right) \frac{P^\alpha}{\sigma_{11}^{(1)} M^\alpha} A_{11} \right]$$

$$+\Gamma \left[\left(d_{21}^\alpha \sigma_{12}^{(2)} - \sigma_{21}^{(2)} d_{12}^\alpha\right) \frac{P^\alpha}{\sigma_{22}^{(2)} M^\alpha} A_{22} - \left(\sigma_{21}^{(2)} F_{12}^\alpha + F_{21}^\alpha \sigma_{12}^{(2)}\right) \frac{1}{\sigma_{22}^{(2)}} \frac{\partial A_{22}}{\partial P^\alpha} \right.$$

$$\left. - \left(\frac{\partial \sigma_{21}^{(2)}}{\partial P^\alpha} F_{12}^\alpha + F_{21}^\alpha \frac{\partial \sigma_{12}^{(2)}}{\partial P^\alpha}\right) \frac{1}{\sigma_{22}^{(2)}} A_{22} + \left(\sigma_{21}^{(2)} F_{12}^\alpha + F_{21}^\alpha \sigma_{12}^{(2)}\right) \frac{1}{\left(\sigma_{22}^{(2)}\right)^2} \frac{\partial \sigma_{22}^{(2)}}{\partial P^\alpha} A_{22} \right]. \qquad (30)$$

Our derivation is almost complete. At this juncture, we are forced to define an off-diagonal nuclear-electronic density matrix, and we do this by sampling the off-diagonal electronic density matrix being carried by our nuclear surface-hopping trajectories. Since different surfaces carry different trajectories, we can form two independent definitions of the off-diagonal full density matrix element

$$A_{12}^{(1)}(\vec{R}, \vec{P}, t) \equiv \frac{\sigma_{12}^{(1)}}{\sigma_{11}^{(1)}} A_{11}$$

$$= \lim_{N_{traj} \to \infty} \frac{1}{N_{traj}} \sum_{traj} \sum_{\lambda_0} \int d\vec{R}_0 \int d\vec{P}_0 \, A_{\lambda_0 \lambda_0}^W(\vec{R}_0, \vec{P}_0) \, \delta(\vec{R}(t; \vec{R}_0, \vec{P}_0, \lambda_0) - \vec{R})$$

$$\times \, \delta(\vec{P}(t; \vec{R}_0, \vec{P}_0, \lambda_0) - \vec{P}) \delta_{\lambda(t),1} \frac{\sigma_{12}^{(1)}(t; \vec{R}_0, \vec{P}_0, \lambda_0)}{\sigma_{11}^{(1)}(t; \vec{R}_0, \vec{P}_0, \lambda_0)}, \tag{31}$$

$$A_{12}^{(2)}(\vec{R}, \vec{P}, t) \equiv \frac{\sigma_{12}^{(2)}}{\sigma_{22}^{(2)}} A_{22}$$

$$= \lim_{N_{traj} \to \infty} \frac{1}{N_{traj}} \sum_{traj} \sum_{\lambda_0} \int d\vec{R}_0 \int d\vec{P}_0 \, A_{\lambda_0 \lambda_0}^W(\vec{R}_0, \vec{P}_0) \, \delta(\vec{R}(t; \vec{R}_0, \vec{P}_0, \lambda_0) - \vec{R})$$

$$\times \, \delta(\vec{P}(t; \vec{R}_0, \vec{P}_0, \lambda_0) - \vec{P}) \delta_{\lambda(t),2} \frac{\sigma_{12}^{(2)}(t; \vec{R}_0, \vec{P}_0, \lambda_0)}{\sigma_{22}^{(2)}(t; \vec{R}_0, \vec{P}_0, \lambda_0)}. \tag{32}$$

Using these definitions, we find

$$\frac{\partial A_{11}(\vec{R}, \vec{P}, t)}{\partial t} \approx -\frac{\partial A_{11}}{\partial R^\alpha} \frac{P^\alpha}{M^\alpha} - \frac{\partial A_{11}}{\partial P^\alpha} F_{11}^\alpha - \Gamma \left[\left(d_{12}^\alpha A_{21}^{(1)} - A_{12}^{(1)} d_{21}^\alpha \right) \frac{P^\alpha}{M^\alpha} \right]$$

$$+ \Gamma \left[\left(d_{21}^\alpha A_{12}^{(2)} - A_{21}^{(2)} d_{12}^\alpha \right) \frac{P^\alpha}{M^\alpha} - \left(\frac{\partial A_{21}^{(2)}}{\partial P^\alpha} F_{12}^\alpha + F_{21}^\alpha \frac{\partial A_{12}^{(2)}}{\partial P^\alpha} \right) \right]. \tag{33}$$

In the second Γ term of Eq. (33), we will assume that the first component usually dominates. After all, interstate coupling terms will be most important near avoided crossings where the derivative coupling $\vec{d}$ is large (in fact, $|\vec{d}| \to \infty$ at a conical intersection). We will call this a minor assumption. Using the identity

$$\Gamma[a + b] = \Theta[a + b] \cdot (a + b) \approx \Theta[a] \cdot (a + b) \qquad \text{for} \qquad |a| \gg |b|, \tag{34}$$

we find

$$\frac{\partial A_{11}(\vec{R}, \vec{P}, t)}{\partial t} \approx -\frac{\partial A_{11}}{\partial R^\alpha} \frac{P^\alpha}{M^\alpha} - \frac{\partial A_{11}}{\partial P^\alpha} F_{11}^\alpha - \Gamma \left[\left(d_{12}^\alpha A_{21}^{(1)} - A_{12}^{(1)} d_{21}^\alpha \right) \frac{P^\alpha}{M^\alpha} \right]$$

$$+ \Gamma \left[\left(d_{21}^\alpha A_{12}^{(2)} - A_{21}^{(2)} d_{12}^\alpha \right) \frac{P^\alpha}{M^\alpha} \right] - \left(\frac{\partial A_{21}^{(2)}}{\partial P^\alpha} F_{12}^\alpha + F_{21}^\alpha \frac{\partial A_{12}^{(2)}}{\partial P^\alpha} \right) \zeta^+, \tag{35}$$

where

$$\zeta^+ = \Theta \left((d_{21}^\alpha A_{12}^{(2)} - A_{21}^{(2)} d_{12}^\alpha) \frac{P^\alpha}{M^\alpha} \right). \tag{36}$$

For future reference, we will also define

$$\zeta^- = \Theta \left(-(d_{21}^\alpha A_{12}^{(2)} - A_{21}^{(2)} d_{12}^\alpha) \frac{P^\alpha}{M^\alpha} \right) \tag{37}$$

with $\zeta^+ + \zeta^- = 1$.

For now, this completes our analysis of the equation of motion for the on-diagonal FSSH full density matrix element.

B. Off-diagonal full density matrix elements

We must now evaluate the equations of motion for the off-diagonal full density matrix elements. Using the chain rule, we find

$$\frac{\partial}{\partial t} A_{12}^{(1)}(\vec{R}, \vec{P}, t) = \frac{\partial \sigma_{12}^{(1)}}{\partial t} \frac{A_{11}}{\sigma_{11}^{(1)}} - \frac{\partial \sigma_{11}^{(1)}}{\partial t} \frac{\sigma_{12}^{(1)}}{(\sigma_{11}^{(1)})^2} A_{11} + \frac{\sigma_{12}^{(1)}}{\sigma_{11}^{(1)}} \frac{\partial A_{11}}{\partial t}. \tag{38}$$

To evaluate the partial time derivatives of the electronic density matrices, we use the common identity for the full hydrodynamic derivative

$$\frac{d\boldsymbol{\sigma}^{(1)}}{dt} = \frac{\partial \boldsymbol{\sigma}^{(1)}}{\partial t} + \frac{\partial \boldsymbol{\sigma}^{(1)}}{\partial R^\alpha} \frac{P^\alpha}{M^\alpha} + \frac{\partial \boldsymbol{\sigma}^{(1)}}{\partial P^\alpha} F_{11}^\alpha$$

$$= \frac{-i}{\hbar}[\mathbf{V}, \boldsymbol{\sigma}^{(1)}] - [\mathbf{d}^\alpha, \boldsymbol{\sigma}^{(1)}]\frac{P^\alpha}{M^\alpha}, \tag{39}$$

$$\Rightarrow \frac{\partial \boldsymbol{\sigma}^{(1)}}{\partial t} = \frac{-i}{\hbar}[\mathbf{V}, \boldsymbol{\sigma}^{(1)}] - [\mathbf{d}^\alpha, \boldsymbol{\sigma}^{(1)}]\frac{P^\alpha}{M^\alpha} - \frac{\partial \boldsymbol{\sigma}^{(1)}}{\partial R^\alpha} \frac{P^\alpha}{M^\alpha} - \frac{\partial \boldsymbol{\sigma}^{(1)}}{\partial P^\alpha} F_{11}^\alpha. \tag{40}$$

Thus,

$$\frac{\partial}{\partial t} A_{12}^{(1)}(\vec{R}, \vec{P}, t) = \left\{ \frac{-i}{\hbar}(V_{11} - V_{22})\sigma_{12}^{(1)} - d_{12}^\alpha(\sigma_{22}^{(1)} - \sigma_{11}^{(1)})\frac{P^\alpha}{M^\alpha} - \frac{\partial \sigma_{12}^{(1)}}{\partial R^\alpha}\frac{P^\alpha}{M^\alpha} - \frac{\partial \sigma_{12}^{(1)}}{\partial P^\alpha}F_{11}^\alpha \right\} \frac{A_{11}}{\sigma_{11}^{(1)}}$$

$$- \left\{ -(d_{12}^\alpha \sigma_{21}^{(1)} - \sigma_{12}^{(1)} d_{21}^\alpha)\frac{P^\alpha}{M^\alpha} - \frac{\partial \sigma_{11}^{(1)}}{\partial R^\alpha}\frac{P^\alpha}{M^\alpha} - \frac{\partial \sigma_{11}^{(1)}}{\partial P^\alpha}F_{11}^\alpha \right\} \frac{\sigma_{12}^{(1)}}{(\sigma_{11}^{(1)})^2} A_{11}$$

$$+ \left\{ -\frac{\partial A_{11}}{\partial R^\alpha}\frac{P^\alpha}{M^\alpha} - \frac{\partial A_{11}}{\partial P^\alpha}F_{11}^\alpha - \Gamma\left[(d_{12}^\alpha A_{21}^{(1)} - A_{12}^{(1)} d_{21}^\alpha)\frac{P^\alpha}{M^\alpha}\right] \right.$$

$$\left. + \Gamma\left[(d_{21}^\alpha A_{12}^{(2)} - A_{21}^{(2)} d_{12}^\alpha)\frac{P^\alpha}{M^\alpha}\right] - \left(\frac{\partial A_{21}^{(2)}}{\partial P^\alpha}F_{12}^\alpha + F_{21}^\alpha \frac{\partial A_{12}^{(2)}}{\partial P^\alpha}\right)\zeta^+ \right\} \frac{\sigma_{12}^{(1)}}{\sigma_{11}^{(1)}}, \tag{41}$$

and after some rearrangement and simplification,

$$\frac{\partial}{\partial t} A_{12}^{(1)}(\vec{R}, \vec{P}, t) = \frac{-i}{\hbar}(V_{11} - V_{22})A_{12}^{(1)} - d_{12}^\alpha \left(\frac{\sigma_{22}^{(1)}}{\sigma_{11}^{(1)}}A_{11} - A_{11}\right)\frac{P^\alpha}{M^\alpha}$$

$$+ \left(-\frac{\partial \sigma_{12}^{(1)}}{\partial R^\alpha}\frac{P^\alpha}{M^\alpha} - \frac{\partial \sigma_{12}^{(1)}}{\partial P^\alpha}F_{11}^\alpha\right)\frac{A_{11}}{\sigma_{11}^{(1)}} - \left(-\frac{\partial \sigma_{11}^{(1)}}{\partial R^\alpha}\frac{P^\alpha}{M^\alpha} - \frac{\partial \sigma_{11}^{(1)}}{\partial P^\alpha}F_{11}^\alpha\right)\frac{\sigma_{12}^{(1)}}{(\sigma_{11}^{(1)})^2}A_{11}$$

$$+ \left(-\frac{\partial A_{11}}{\partial R^\alpha}\frac{P^\alpha}{M^\alpha} - \frac{\partial A_{11}}{\partial P^\alpha}F_{11}^\alpha\right)\frac{\sigma_{12}^{(1)}}{\sigma_{11}^{(1)}} + (d_{12}^\alpha \sigma_{21}^{(1)} - \sigma_{12}^{(1)} d_{21}^\alpha)\frac{P^\alpha}{M^\alpha}\frac{\sigma_{12}^{(1)}}{(\sigma_{11}^{(1)})^2}A_{11}$$

$$+ \left\{ -\Gamma\left[(d_{12}^\alpha A_{21}^{(1)} - A_{12}^{(1)} d_{21}^\alpha)\frac{P^\alpha}{M^\alpha}\right] + \Gamma\left[(d_{21}^\alpha A_{12}^{(2)} - A_{21}^{(2)} d_{12}^\alpha)\frac{P^\alpha}{M^\alpha}\right] \right\} \frac{\sigma_{12}^{(1)}}{\sigma_{11}^{(1)}}$$

$$- \left(\frac{\partial A_{21}^{(2)}}{\partial P^\alpha}F_{12}^\alpha + F_{21}^\alpha \frac{\partial A_{12}^{(2)}}{\partial P^\alpha}\right)\frac{\sigma_{12}^{(1)}}{\sigma_{11}^{(1)}}\zeta^+ \tag{42}$$

$$= \frac{-i}{\hbar}(V_{11} - V_{22})A_{12}^{(1)} - d_{12}^\alpha \left(\frac{\sigma_{22}^{(1)}}{\sigma_{11}^{(1)}}A_{11} - A_{11}\right)\frac{P^\alpha}{M^\alpha}$$

$$- \left(\frac{\partial A_{12}^{(1)}}{\partial R^\alpha}\frac{P^\alpha}{M^\alpha} + \frac{\partial A_{12}^{(1)}}{\partial P^\alpha}F_{11}^\alpha\right) + (d_{12}^\alpha \sigma_{21}^{(1)} - \sigma_{12}^{(1)} d_{21}^\alpha)\frac{P^\alpha}{M^\alpha}\frac{\sigma_{12}^{(1)}}{(\sigma_{11}^{(1)})^2}A_{11}$$

$$+ \left\{ -\Gamma\left[(d_{12}^\alpha A_{21}^{(1)} - A_{12}^{(1)} d_{21}^\alpha)\frac{P^\alpha}{M^\alpha}\right] + \Gamma\left[(d_{21}^\alpha A_{12}^{(2)} - A_{21}^{(2)} d_{12}^\alpha)\frac{P^\alpha}{M^\alpha}\right] \right\} \frac{\sigma_{12}^{(1)}}{\sigma_{11}^{(1)}}$$

$$- \left(\frac{\partial A_{21}^{(2)}}{\partial P^\alpha}F_{12}^\alpha + F_{21}^\alpha \frac{\partial A_{12}^{(2)}}{\partial P^\alpha}\right)\frac{\sigma_{12}^{(1)}}{\sigma_{11}^{(1)}}\zeta^+. \tag{43}$$

C. Consistency of equations: Part 1

In Eqs. (31) and (32), we have defined two separate off-diagonal matrix elements. In the spirit of Tully's self-consistency equation (Eq. (18)), let us now make three large assumptions about the consistency of these definitions at time t (and later we will show how to maintain this consistency at longer times),

$$A_{12}^{(1)} = A_{12}^{(2)}, \tag{44}$$

$$A_{11}\sigma_{22}^{(1)} = A_{22}\sigma_{11}^{(1)}, \tag{45}$$

$$A_{11}\sigma_{22}^{(2)} = A_{22}\sigma_{11}^{(2)}. \tag{46}$$

Other conditions emerge naturally from these three conditions. For instance, dividing Eq. (45) by Eq. (44) leads to

$$\frac{\sigma_{12}^{(1)}}{\sigma_{22}^{(1)}} = \frac{\sigma_{12}^{(2)}}{\sigma_{22}^{(2)}}. \tag{47}$$

With these assumptions, we find (recalling that $\Gamma[x] - \Gamma[-x] = x$ so three terms cancel in Eq. (43)),

$$\frac{\partial A_{11}(\vec{R}, \vec{P}, t)}{\partial t}$$

$$= -(d_{12}^{\alpha} A_{21}^{(1)} - A_{12}^{(1)} d_{21}^{\alpha})\frac{P^{\alpha}}{M^{\alpha}} - \frac{\partial A_{11}}{\partial R^{\alpha}}\frac{P^{\alpha}}{M^{\alpha}} - \frac{\partial A_{11}}{\partial P^{\alpha}}F_{11}^{\alpha}$$

$$- \left(\frac{\partial A_{12}^{(2)}}{\partial P^{\alpha}}F_{21}^{\alpha} + F_{12}^{\alpha}\frac{\partial A_{21}^{(2)}}{\partial P^{\alpha}}\right)\zeta^{+}, \tag{48}$$

$$\frac{\partial}{\partial t}A_{12}^{(1)}(\vec{R}, \vec{P}, t)$$

$$= \frac{-i}{\hbar}(V_{11} - V_{22})A_{12}^{(1)}$$

$$- \frac{P^{\alpha}}{M^{\alpha}}d_{12}^{\alpha}(A_{22} - A_{11}) - \frac{P^{\alpha}}{M^{\alpha}}\frac{\partial A_{12}^{(1)}}{\partial R^{\alpha}}$$

$$- F_{11}^{\alpha}\frac{\partial A_{12}^{(1)}}{\partial P^{\alpha}} - \left(\frac{\partial A_{21}^{(2)}}{\partial P^{\alpha}}F_{12}^{\alpha} + F_{21}^{\alpha}\frac{\partial A_{12}^{(2)}}{\partial P^{\alpha}}\right)\frac{\sigma_{12}^{(1)}}{\sigma_{11}^{(1)}}\zeta^{+}, \tag{49}$$

and similarly

$$\frac{\partial}{\partial t}A_{12}^{(2)}(\vec{R}, \vec{P}, t)$$

$$= \frac{-i}{\hbar}(V_{11} - V_{22})A_{12}^{(2)}$$

$$- \frac{P^{\alpha}}{M^{\alpha}}d_{12}^{\alpha}(A_{22} - A_{11}) - \frac{P^{\alpha}}{M^{\alpha}}\frac{\partial A_{12}^{(2)}}{\partial R^{\alpha}}$$

$$- F_{22}^{\alpha}\frac{\partial A_{12}^{(2)}}{\partial P^{\alpha}} - \left(\frac{\partial A_{21}^{(1)}}{\partial P^{\alpha}}F_{12}^{\alpha} + F_{21}^{\alpha}\frac{\partial A_{12}^{(1)}}{\partial P^{\alpha}}\right)\frac{\sigma_{12}^{(2)}}{\sigma_{22}^{(2)}}\zeta^{-}. \tag{50}$$

Comparing Eq. (48) with Eq. (3), we find some good news: these equations are quite similar, except for the factor of 1/2 in Eq. (3) that is replaced by the Heaviside function ζ^{+} in Eq. (48). Luckily, there are two important cases where

this difference will not be important: (1) first and most obviously, if the off-diagonal force F_{12} term is weak, so that the $\vec{F}_{12}\cdot$ Re $(\frac{\partial A_{21}}{\partial \vec{P}})$ term in Eq. (48) is small and negligible compared to the $(\vec{d}_{12}\cdot\frac{\vec{P}}{M})$ Re (A_{21}) term for describing hops; (2) second, if the $\vec{F}_{12}\cdot$ Re $(\frac{\partial A_{21}}{\partial \vec{P}})$ term is uncorrelated with the $(\vec{d}_{12}\cdot\frac{\vec{P}}{M})$ Re(A_{21}) term, and the latter undergoes many oscillations over long stretches of time as the nuclei meander in a region of crossing (as will be common in high dimensional systems with friction). For this reason, we will label the 1/2 vs. ζ^{+} discrepancy as a minor limitation (compared with the major assumptions required elsewhere in this paper).

1. Major condition #3: Modified electronic propagation that includes decoherence

However, comparing Eqs. (49) and (50), we find two pieces of apparently bad news: (1) if $A_{12}^{(1)}$ and $A_{12}^{(2)}$ are equal at time t, they will not be equal at any time later because they have different derivatives; and (2) neither density $A_{12}^{(1)}$ or $A_{12}^{(2)}$ agrees with the equation of motion from the QCLE (Eq. (4)). That being said, though, Eqs. (49) and (50) can be roughly corrected by altering the time-dependent electronic Schrödinger equation (Eq. (11)) as follows:

$$\dot{\sigma}_{12}^{(1)} = \frac{-i}{\hbar}(V_{11} - V_{22})\sigma_{12}^{(1)} - d_{12}^{\alpha}(\sigma_{22}^{(1)} - \sigma_{11}^{(1)})\frac{P^{\alpha}}{M^{\alpha}} - \gamma_{12}^{(1)}\sigma_{12}^{(1)} \tag{51}$$

and

$$\dot{\sigma}_{12}^{(2)} = \frac{-i}{\hbar}(V_{11} - V_{22})\sigma_{12}^{(2)} - d_{12}^{\alpha}(\sigma_{22}^{(2)} - \sigma_{11}^{(2)})\frac{P^{\alpha}}{M^{\alpha}} - \gamma_{12}^{(2)}\sigma_{12}^{(2)}. \tag{52}$$

Using Eqs. (51) and (52), the swarm of trajectories has a new equation of motion for the off-diagonal matrix element

$$\frac{\partial}{\partial t}A_{12}^{(1)}(R, P, t)$$

$$= -\gamma_{12}^{(1)}A_{12}^{(1)} - \frac{i}{\hbar}(V_{11} - V_{22})A_{12}^{(1)}$$

$$- \frac{P^{\alpha}}{M^{\alpha}}d_{12}^{\alpha}(A_{22} - A_{11}) - \frac{P^{\alpha}}{M^{\alpha}}\frac{\partial A_{12}^{(1)}}{\partial R^{\alpha}}$$

$$- F_{11}^{\alpha}\frac{\partial A_{12}^{(1)}}{\partial P^{\alpha}} - \left(\frac{\partial A_{21}^{(2)}}{\partial P^{\alpha}}F_{12}^{\alpha} + F_{21}^{\alpha}\frac{\partial A_{12}^{(2)}}{\partial P^{\alpha}}\right)\frac{\sigma_{12}^{(1)}}{\sigma_{11}^{(1)}}\zeta^{+}, \tag{53}$$

$$\frac{\partial}{\partial t}A_{12}^{(2)}(R, P, t)$$

$$= -\gamma_{12}^{(2)}A_{12}^{(2)} - \frac{i}{\hbar}(V_{11} - V_{22})A_{12}^{(2)}$$

$$- \frac{P^{\alpha}}{M^{\alpha}}d_{12}^{\alpha}(A_{22} - A_{11}) - \frac{P^{\alpha}}{M^{\alpha}}\frac{\partial A_{12}^{(2)}}{\partial R^{\alpha}}$$

$$- F_{22}^{\alpha}\frac{\partial A_{12}^{(2)}}{\partial P^{\alpha}} - \left(\frac{\partial A_{21}^{(1)}}{\partial P^{\alpha}}F_{12}^{\alpha} + F_{21}^{\alpha}\frac{\partial A_{12}^{(1)}}{\partial P^{\alpha}}\right)\frac{\sigma_{12}^{(2)}}{\sigma_{22}^{(2)}}\zeta^{-}. \tag{54}$$

Comparing Eqs. (53) and (54) with Eq. (4), we find that, for the correct QCLE dynamics, we must have (using

Eq. (47)),

$$\gamma_{12}^{(1)} = \frac{1}{2}\left(F_{22}^\alpha - F_{11}^\alpha\right)\frac{1}{A_{12}^{(1)}}\frac{\partial A_{12}^{(1)}}{\partial P^\alpha} - \frac{\zeta^+}{A_{12}^{(1)}}\left(\frac{\partial A_{21}^{(2)}}{\partial P^\alpha}F_{12}^\alpha + F_{21}^\alpha\frac{\partial A_{12}^{(2)}}{\partial P^\alpha}\right)\frac{\sigma_{12}^{(1)}}{\sigma_{11}^{(1)}} + \frac{1}{2A_{12}^{(1)}}F_{12}^\alpha\left(\frac{\partial A_{11}}{\partial P^\alpha} + \frac{\partial A_{22}}{\partial P^\alpha}\right) \tag{55}$$

$$= \frac{1}{2}\left(F_{22}^\alpha - F_{11}^\alpha\right)\frac{1}{A_{12}^{(1)}}\frac{\partial A_{12}^{(1)}}{\partial P^\alpha} - \frac{\zeta^+}{A_{12}^{(1)}}\left(\frac{\partial A_{21}^{(2)}}{\partial P^\alpha}F_{12}^\alpha + F_{21}^\alpha\frac{\partial A_{12}^{(2)}}{\partial P^\alpha}\right)\frac{\sigma_{12}^{(1)}}{\sigma_{11}^{(1)}} + \frac{1}{2\sigma_{12}^{(1)}}F_{12}^\alpha\left(\frac{\sigma_{11}^{(1)}}{A_{11}}\frac{\partial A_{11}}{\partial P^\alpha} + \frac{\sigma_{22}^{(1)}}{A_{22}}\frac{\partial A_{22}}{\partial P^\alpha}\right) \tag{56}$$

and

$$\gamma_{12}^{(2)} = \frac{1}{2}\left(F_{11}^\alpha - F_{22}^\alpha\right)\frac{1}{A_{12}^{(2)}}\frac{\partial A_{12}^{(2)}}{\partial P^\alpha} - \frac{\zeta^-}{A_{12}^{(2)}}\left(\frac{\partial A_{21}^{(1)}}{\partial P^\alpha}F_{12}^\alpha + F_{21}^\alpha\frac{\partial A_{12}^{(1)}}{\partial P^\alpha}\right)\frac{\sigma_{12}^{(2)}}{\sigma_{22}^{(2)}} + \frac{1}{2\sigma_{12}^{(2)}}F_{12}^\alpha\left(\frac{\sigma_{11}^{(2)}}{A_{11}}\frac{\partial A_{11}}{\partial P^\alpha} + \frac{\sigma_{22}^{(2)}}{A_{22}}\frac{\partial A_{22}}{\partial P^\alpha}\right). \tag{57}$$

The equations above incorporate necessary corrections to the electron density matrix equations of motion that must be implemented for FSSH trajectories to agree with QCLE dynamics. More specifically, if we substitute Eqs. (51) and (52) in place of Eq. (11), then we will find that $A_{12}^{(1)}$ and $A_{12}^{(2)}$ have the same equation of motion, namely, Eq. (4) for the QCLE. Thus, we now find:

- Condition #3 (option #a) for FSSH to match QCLE dynamics: the electronic Schrödinger equation must be altered according to Eqs. (55)–(57).

There is one special case that deserves mention, whereby it is easy to interpret the meaning of these corrections to the electronic Schrödinger equation. Consider the case when the interstate forces F_{12}^α are small on average so that the last two terms in Eqs. (55)–(57) can be ignored. In practice, this likely means that interstate transitions should be dictated by the dynamics at sharply avoided crossings, where the derivative couplings are dominant; interstate transitions should not be smeared out over large regions of configuration space where the interstate forces F_{12}^α can be small but cumulatively large. This approximation gives:

- Condition #3 (option #b) for FSSH to match QCLE dynamics: when applicable, the electronic Schrödinger equation can be altered according to Eqs. (58) and (59),

$$\gamma_{12}^{(1)} \approx \frac{1}{2}\left(F_{22}^\alpha - F_{11}^\alpha\right)\frac{1}{A_{12}^{(1)}}\frac{\partial A_{12}^{(1)}}{\partial P^\alpha}, \tag{58}$$

$$\gamma_{12}^{(2)} \approx \frac{1}{2}\left(F_{11}^\alpha - F_{22}^\alpha\right)\frac{1}{A_{12}^{(2)}}\frac{\partial A_{12}^{(2)}}{\partial P^\alpha}. \tag{59}$$

Observe that in Eqs. (58) and (59), assuming the sign of γ_{12} is positive for each trajectory, the off-diagonal elements of the

electronic density matrix must be damped. Thus, physically, condition #3 incorporates the fact that the standard FSSH algorithm is "overly coherent" and requires a decoherence correction; furthermore, that decoherence correction must be proportional to the difference in adiabatic forces, $(\vec{F}_{11} - \vec{F}_{22})$.

Very roughly speaking, the decoherence rate in Eqs. (58) and (59) was chosen by Neria and Nitzan[46] and Rossky, Schwartz, and Prezhdo[12,13] using a frozen Gaussian ansatz: this rate corresponds to two nuclear wave packets moving apart on different surfaces. Interestingly, with our collaborator Neil Shenvi, we found almost the same decoherence rate *without* a frozen Gaussian ansatz: compare Eq. (58) from this paper with Eq. (33) in Ref. 48. We will discuss decoherence further in Sec. III E.

D. Consistency of equations: Part 2

Thus far, we have shown that if $A_{12}^{(1)} = A_{12}^{(2)}$ at time t, then we can insist that $A_{12}^{(1)} = A_{12}^{(2)}$ at later times simply by damping the off-diagonal electronic density matrix elements σ_{12}. For this reason, we will now drop the superscript from A_{12}, $A_{12} \equiv A_{12}^{(1)} \equiv A_{12}^{(2)}$. The only item left is to ensure that if $A_{11}\sigma_{22}^{(1)} = A_{22}\sigma_{11}^{(1)}$ at time t, then this will also be true at later times. (The same argument should also work as far as insisting that $A_{11}\sigma_{22}^{(2)} = A_{22}\sigma_{11}^{(2)}$.)

To ensure this consistency, we will add an extra damping term to the equation of motion for the on-diagonal (but inactive) electronic density matrix element (i.e., Eq. (10)). Without loss of generality, suppose that surface 1 is active:

$$\frac{d}{dt}\sigma_{22}^{(1)}(t) = -\frac{P^\alpha}{M^\alpha}\left(d_{21}^\alpha\sigma_{12}^{(1)} - \sigma_{21}^{(1)}d_{12}^\alpha\right) - \gamma_{22}^{(1)}\sigma_{22}^{(1)}. \tag{60}$$

Consider now the partial time derivative of both sides of $\frac{\partial}{\partial t}(A_{11}\sigma_{22}^{(1)}) = \frac{\partial}{\partial t}(A_{22}\sigma_{11}^{(1)})$. Differentiating, we find

$$\left\{-\frac{\partial A_{11}}{\partial R^\alpha}\frac{P^\alpha}{M^\alpha} - \frac{\partial A_{11}}{\partial P^\alpha}F_{11}^\alpha - (A_{21}d_{12}^\alpha - d_{21}^\alpha A_{12})\frac{P^\alpha}{M^\alpha} - \left(\frac{\partial A_{21}}{\partial P^\alpha}F_{12}^\alpha + F_{21}^\alpha\frac{\partial A_{12}}{\partial P^\alpha}\right)\zeta^+\right\}\sigma_{22}^{(1)}$$

$$+ A_{11}\left\{-(d_{21}^\alpha\sigma_{12}^{(1)} - d_{12}^\alpha\sigma_{21}^{(1)})\frac{P^\alpha}{M^\alpha} - \frac{\partial\sigma_{22}^{(1)}}{\partial R^\alpha}\frac{P^\alpha}{M^\alpha} - \frac{\partial\sigma_{22}^{(1)}}{\partial P^\alpha}F_{11}^\alpha - \gamma_{22}^{(1)}\sigma_{22}^{(1)}\right\}$$

$$
= \left\{ -\frac{\partial A_{22}}{\partial R^\alpha} \frac{P^\alpha}{M^\alpha} - \frac{\partial A_{22}}{\partial P^\alpha} F_{22}^\alpha - (A_{12} d_{21}^\alpha - d_{12}^\alpha A_{21}) \frac{P^\alpha}{M^\alpha} - \left(\frac{\partial A_{12}}{\partial P^\alpha} F_{21}^\alpha + F_{12}^\alpha \frac{\partial A_{21}}{\partial P^\alpha} \right) \zeta^- \right\} \sigma_{11}^{(1)}
$$

$$
+ A_{22} \left\{ -(d_{12}^\alpha \sigma_{21}^{(1)} - d_{21}^\alpha \sigma_{12}^{(1)}) \frac{P^\alpha}{M^\alpha} - \frac{\partial \sigma_{11}^{(1)}}{\partial R^\alpha} \frac{P^\alpha}{M^\alpha} - \frac{\partial \sigma_{11}^{(1)}}{\partial P^\alpha} F_{11}^\alpha \right\}. \tag{61}
$$

If we plug in $A_{11} = \frac{A_{22} \sigma_{11}^{(1)}}{\sigma_{22}^{(1)}}$ and evaluate the derivatives in the first term,

$$
\frac{\partial A_{11}}{\partial R^\alpha} = \frac{\partial \left(\frac{A_{22} \sigma_{11}^{(1)}}{\sigma_{22}^{(1)}} \right)}{\partial R^\alpha} = \frac{\sigma_{11}^{(1)}}{\sigma_{22}^{(1)}} \frac{\partial A_{22}}{\partial R^\alpha} + \frac{A_{22}}{\sigma_{22}^{(1)}} \frac{\partial \sigma_{11}^{(1)}}{\partial R^\alpha} - \frac{\sigma_{11}^{(1)} A_{22}}{(\sigma_{22}^{(1)})^2} \frac{\partial \sigma_{22}^{(1)}}{\partial R^\alpha}, \tag{62}
$$

$$
\frac{\partial A_{11}}{\partial P^\alpha} = \frac{\partial \left(\frac{A_{22} \sigma_{11}^{(1)}}{\sigma_{22}^{(1)}} \right)}{\partial P^\alpha} = \frac{\sigma_{11}^{(1)}}{\sigma_{22}^{(1)}} \frac{\partial A_{22}}{\partial P^\alpha} + \frac{A_{22}}{\sigma_{22}^{(1)}} \frac{\partial \sigma_{11}^{(1)}}{\partial P^\alpha} - \frac{\sigma_{11}^{(1)} A_{22}}{(\sigma_{22}^{(1)})^2} \frac{\partial \sigma_{22}^{(1)}}{\partial P^\alpha}, \tag{63}
$$

we find a seemingly very complicated equation,

$$
- \left\{ \frac{\sigma_{11}^{(1)}}{\sigma_{22}^{(1)}} \frac{\partial A_{22}}{\partial R^\alpha} + \frac{A_{22}}{\sigma_{22}^{(1)}} \frac{\partial \sigma_{11}^{(1)}}{\partial R^\alpha} - \frac{\sigma_{11}^{(1)} A_{22}}{(\sigma_{22}^{(1)})^2} \frac{\partial \sigma_{22}^{(1)}}{\partial R^\alpha} \right\} \frac{P^\alpha}{M^\alpha} \sigma_{22}^{(1)}
$$

$$
- \left\{ \frac{\sigma_{11}^{(1)}}{\sigma_{22}^{(1)}} \frac{\partial A_{22}}{\partial P^\alpha} + \frac{A_{22}}{\sigma_{22}^{(1)}} \frac{\partial \sigma_{11}^{(1)}}{\partial P^\alpha} - \frac{\sigma_{11}^{(1)} A_{22}}{(\sigma_{22}^{(1)})^2} \frac{\partial \sigma_{22}^{(1)}}{\partial P^\alpha} \right\} F_{11}^\alpha \sigma_{22}^{(1)}
$$

$$
+ \left\{ -(A_{21} d_{12}^\alpha - d_{21}^\alpha A_{12}) \frac{P^\alpha}{M^\alpha} - \left(\frac{\partial A_{21}}{\partial P^\alpha} F_{12}^\alpha + F_{21}^\alpha \frac{\partial A_{12}}{\partial P^\alpha} \right) \zeta^+ \right\} \sigma_{22}^{(1)}
$$

$$
+ \frac{A_{22} \sigma_{11}^{(1)}}{\sigma_{22}^{(1)}} \left\{ -(d_{21}^\alpha \sigma_{12}^{(1)} - d_{12}^\alpha \sigma_{21}^{(1)}) \frac{P^\alpha}{M^\alpha} - \frac{\partial \sigma_{22}^{(1)}}{\partial R^\alpha} \frac{P^\alpha}{M^\alpha} - \frac{\partial \sigma_{22}^{(1)}}{\partial P^\alpha} F_{11}^\alpha - \gamma_{22}^{(1)} \sigma_{22}^{(1)} \right\}
$$

$$
= \left\{ -\frac{\partial A_{22}}{\partial R^\alpha} \frac{P^\alpha}{M^\alpha} - \frac{\partial A_{22}}{\partial P^\alpha} F_{22}^\alpha - (A_{12} d_{21}^\alpha - d_{12}^\alpha A_{21}) \frac{P^\alpha}{M^\alpha} - \left(\frac{\partial A_{12}}{\partial P^\alpha} F_{21}^\alpha + F_{12}^\alpha \frac{\partial A_{21}}{\partial P^\alpha} \right) \zeta^- \right\} \sigma_{11}^{(1)}
$$

$$
+ A_{22} \left\{ -(d_{12}^\alpha \sigma_{21}^{(1)} - d_{21}^\alpha \sigma_{12}^{(1)}) \frac{P^\alpha}{M^\alpha} - \frac{\partial \sigma_{11}^{(1)}}{\partial R^\alpha} \frac{P^\alpha}{M^\alpha} - \frac{\partial \sigma_{11}^{(1)}}{\partial P^\alpha} F_{11}^\alpha \right\}. \tag{64}
$$

However, there is in fact a massive cancellation of terms, leading to

$$
- \sigma_{11}^{(1)} \frac{\partial A_{22}}{\partial P^\alpha} F_{11}^\alpha - \left(\frac{\partial A_{21}}{\partial P^\alpha} F_{12}^\alpha + F_{21}^\alpha \frac{\partial A_{12}}{\partial P^\alpha} \right) \sigma_{22}^{(1)} \zeta^+ - \gamma_{22}^{(1)} \sigma_{11}^{(1)} A_{22}
$$

$$
= - \sigma_{11}^{(1)} \frac{\partial A_{22}}{\partial P^\alpha} F_{22}^\alpha - \left(\frac{\partial A_{12}}{\partial P^\alpha} F_{21}^\alpha + F_{12}^\alpha \frac{\partial A_{21}}{\partial P^\alpha} \right) \sigma_{11}^{(1)} \zeta^-, \tag{65}
$$

or, rearranging,

$$
\gamma_{22}^{(1)} = (F_{22}^\alpha - F_{11}^\alpha) \frac{1}{A_{22}} \frac{\partial A_{22}}{\partial P^\alpha} + \left(\frac{\zeta^- \sigma_{11}^{(1)} - \zeta^+ \sigma_{22}^{(1)}}{\sigma_{11}^{(1)} A_{22}} \right) \left(\frac{\partial A_{21}}{\partial P^\alpha} F_{12}^\alpha + F_{21}^\alpha \frac{\partial A_{12}}{\partial P^\alpha} \right) \tag{66}
$$

$$
= (F_{22}^\alpha - F_{11}^\alpha) \frac{1}{A_{22}} \frac{\partial A_{22}}{\partial P^\alpha} + \left(\frac{\zeta^- \sigma_{11}^{(1)} - \zeta^+ \sigma_{22}^{(1)}}{\sigma_{22}^{(1)} A_{11}} \right) \left(\frac{\partial A_{21}}{\partial P^\alpha} F_{12}^\alpha + F_{21}^\alpha \frac{\partial A_{12}}{\partial P^\alpha} \right). \tag{67}
$$

If we consider the case (as above) that the off-diagonal forces are small, then we can ignore the second term, and we find

$$\gamma_{22}^{(1)} \approx \left(F_{22}^\alpha - F_{11}^\alpha \right) \frac{1}{A_{22}} \frac{\partial A_{22}}{\partial P^\alpha}. \tag{68}$$

Thus, we find that, for each trajectory, we should also be damping the on-diagonal density matrix element for the non-active surfaces (assuming the term on the right hand side of Eq. (68) is positive). Of course, we can also apply the corresponding damping terms for trajectories that move along surface 2, thus ensuring that $A_{11}\sigma_{22}^{(2)} = A_{22}\sigma_{11}^{(2)}$.

In the end, this damping requires that (if $\lambda = 1$ is the active surface)

$$\lim_{t \to \infty} \boldsymbol{\sigma}^{(1)}(t) \propto \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}. \tag{69}$$

In words, this means that the electronic density matrix must eventually return to the electronically pure active adiabatic state.

E. Decoherence by collapse, frozen Gaussian ansatz, and the A-FSSH approximation

At this point, we have shown that Tully's FSSH algorithm can be derived if we make several major and minor assumptions, including an adjustment for the equation of motion of the electronic density matrix. Focusing on the latter requirement, however, we might well find that a direct implementation of Eqs. (51), (52), and (60) with γ from Eqs. (55)–(57) and (66) has several drawbacks (option #a). One problem is that the resulting equations will not maintain purity of the density matrix and hence will likely be unstable. For instance, if $\gamma_{12}^{(1)}$ or $\gamma_{22}^{(1)}$ is negative, then the corresponding matrix elements are enhanced (rather than damped) and can grow exponentially. Indeed, one reason for the stability of FSSH is that the algorithm propagates trajectories with pure electronic states (not mixed states). As such, there is never a chance of finding an electronic density matrix with negative eigenvalues (for example). Indeed, propagating FSSH dynamics with mixed electronic density matrices would barely resemble the original FSSH algorithm. As an alternative, it might make sense to implement only the positive damping piece of these equations which is effectively an implementation of decoherence. We will now define options #c and #d pertaining to condition #3 for FSSH to match QCLE dynamics:

- Condition #3 (option #c): when applicable, the electronic Schrödinger equation can be corrected according to Eqs. (55)–(57), (66) with the restriction that we make corrections only when the damping term is positive.
- Condition #3 (option #d): when applicable, the electronic Schrödinger equation can be corrected according to Eqs. (58), (59), (68) with the restriction that we make corrections only when the damping term is positive.

We emphasize that we are far from the first researchers to follow this line of thinking. In surface-hopping papers published more than a decade ago, Rossky, Schwartz, and Prezhdo[12, 13] faced the decoherence problem in FSSH and the failure of the algorithm to allow full wave packet separation. As a remedy, the authors suggested a modification of FSSH by collapsing the electronic amplitude with some prescribed decoherence rate.[12, 13] Just as we are now proposing, the authors needed to modify the electronic Schrödinger equation to incorporate decoherence directly, so they chose discontinuous collapsing events for reasons of stability. Another option would have been continuous amplitude damping, i.e.,

$$\frac{dc_2^{(1)}}{dt} = -\frac{i}{\hbar} V_{22} c_2^{(1)} - \frac{P^\alpha}{M^\alpha} d_{21}^\alpha c_1^{(1)} - \gamma_2^{(1)} c_2^{(1)}. \tag{70}$$

Hammes-Schiffer, Truhlar, Granucci, and co-workers[14–21,49,52] have proposed similar schemes over the last few years. The contribution of this paper is that we now understand exactly how the time-dependent electronic Schrödinger equation should be modified and we can further quantify the limitations of implementing only decoherence.

Now, if we decide to modify the time-dependent Schrödinger equation for decoherence only, the next question is: how can we implement the decoherence rate in Eqs. (58), (59), and (68) most effectively? Formally, this damping equation no longer allows independent FSSH trajectories. Instead, at every time step, one would need to average over all trajectories and estimate $\frac{1}{A_{22}} \frac{\partial A_{22}}{\partial P^\alpha}$ and $\frac{1}{A_{12}} \frac{\partial A_{12}}{\partial P^\alpha}$ on the fly at all points in phase space where a trajectory sits. This approach will need to be tested in the future. Alternatively, one could attempt to integrate $\frac{1}{A_{22}} \frac{\partial A_{22}}{\partial P^\alpha}$ and $\frac{1}{A_{12}} \frac{\partial A_{12}}{\partial P^\alpha}$ forward in time along a trajectory, but there are no simple closed equations to do so.

Over the last few years, our research group has pioneered a new algorithm entitled augmented FSSH (A-FSSH).[27,48] The general premise is to calculate moments[53–58] of the total nuclear-electronic wavefunction relative to a surface-hopping trajectory, and then use those moments to collapse the density matrix (à la condition #3's option #d above). In the language of Ref. 27, we calculate $\Delta \vec{R}$ and $\Delta \vec{P}$ and, interestingly, the off-diagonal momentum moment in A-FSSH ($\Delta \vec{P}_{12}$) is propagated along the mean potential $\frac{1}{2}(\vec{F}_{11} + \vec{F}_{22})$ just as A_{12}^W is propagated in the QCLE. Further work on this connection is underway currently, but thus far, we have been able to justify our A-FSSH implementation only through a frozen Gaussian interpretation.[59]

From the perspective of frozen Gaussians, an electronically relaxing wavefunction can be approximated as

$$\Psi(\vec{r}, \vec{R}, t) = c_1 g(\vec{R}; \vec{R}_1(t), \vec{P}_1(t)) \Phi_1(\vec{r}; \vec{R})$$
$$+ c_2 g(\vec{R}; \vec{R}_2(t), \vec{P}_2(t)) \Phi_2(\vec{r}; \vec{R}), \tag{71}$$

where

$$g(\vec{R}; \vec{R}_s(t), \vec{P}_s(t)) \equiv \prod_\alpha \left(\frac{1}{\pi a_{R^\alpha}^2} \right)^{1/4} \exp\left(\frac{-(R^\alpha - R_s^\alpha(t))^2}{2a_{R^\alpha}^2} \right)$$
$$\times \exp\left(\frac{i}{\hbar} P_s^\alpha(t)(R^\alpha - R_s^\alpha(t)) \right). \tag{72}$$

In this case, one finds that

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

$$\times \exp\left(\frac{-(P^\alpha - P_2^\alpha)^2 a_{R^\alpha}^2}{\hbar^2}\right), \qquad (73)$$

$$A_{12}(\vec{R}, \vec{P}) = \frac{c_1 c_2^*}{(\pi\hbar)^{3N}} \prod_\alpha \exp\left(\frac{-\left(R^\alpha - \frac{1}{2}(R_2^\alpha + R_1^\alpha)\right)^2}{a_{R^\alpha}^2}\right)$$

$$\times \exp\left(\frac{-\left(P^\alpha - \frac{1}{2}(P_2^\alpha + P_1^\alpha)\right)^2 a_{R^\alpha}^2}{\hbar^2}\right)$$

$$\times \exp\left(\frac{i(R_2^\alpha - R_1^\alpha)P^\alpha}{\hbar}\right) \exp\left(\frac{i(P_1^\alpha - P_2^\alpha)R^\alpha}{\hbar}\right)$$

$$\times \exp\left(\frac{i(P_2^\alpha - P_1^\alpha)(R_2^\alpha + R_1^\alpha)}{2\hbar}\right). \qquad (74)$$

When we are following a trajectory on surface 1, a further simplification would be to evaluate these expressions at $(\vec{R}_1, \vec{P}_1)$, leading to the equalities

$$\frac{1}{A_{22}}\frac{\partial A_{22}}{\partial P^\alpha}\bigg|_{\vec{P}=\vec{P}_1} = -2\frac{(P_1^\alpha - P_2^\alpha)a_{R^\alpha}^2}{\hbar^2}, \qquad (75)$$

$$\frac{1}{2}\text{Re}\left(\frac{1}{A_{12}}\frac{\partial A_{12}}{\partial P^\alpha}\bigg|_{\vec{P}=\vec{P}_1}\right) = -\frac{1}{2}\frac{(P_1^\alpha - P_2^\alpha)a_{R^\alpha}^2}{\hbar^2}, \quad (76)$$

$$\Rightarrow \gamma_{22}^{(1)} \approx 4\gamma_{12}^{(1)}. \qquad (77)$$

Thus, according to Eqs. (58) and (76), in the limit of a frozen Gaussian wavefunction, the off-diagonal density matrix element should decay with the approximate rate

$$\frac{1}{\tau} = \frac{a_{R^\alpha}^2}{2\hbar^2}(P_1^\alpha - P_2^\alpha)(F_1^\alpha - F_2^\alpha). \qquad (78)$$

For comparison, note that the decay of the overlap matrix element[12,13,46] between frozen Gaussians is

$$\frac{1}{\tau_{overlap}^{FG}} = \frac{1}{2M^\alpha a_{R^\alpha}^2}(R_1^\alpha - R_2^\alpha)(P_1^\alpha - P_2^\alpha)$$

$$+ \frac{a_{R^\alpha}^2}{2\hbar^2}(P_1^\alpha - P_2^\alpha)(F_1^\alpha - F_2^\alpha). \qquad (79)$$

Hence, the rigorous decoherence correction found in this paper matches only one term (the momentum term) of the frozen Gaussian expression. In fact, the decoherence rate for the A-FSSH algorithm is equivalent to Eq. (78) (see Eq. (44) in Ref. 48). In the Appendix, we briefly review how a width parameter a_{R^α} can be estimated quasi-variationally.

We close this section with a few words about decoherence and collapsing. According to Eq. (77), within a frozen Gaussian ansatz, there are actually two different damping rates for the electronic density matrix that differ by a factor of four, one for the on-diagonal and one for the off-diagonal matrix element. Normally, if we were to damp the non-active amplitude (as in Eq. (70)), we would expect diagonal and off-diagonal damping rates to differ naturally by a factor of two,

i.e., $\gamma_{22}^{(1)} = 2\gamma_{12}^{(1)} = 2\gamma_2^{(1)}$. Thus, the expression in Eq. (77) almost corresponds to amplitude damping, except for a factor of two. This difference in factors highlights the approximation inherent in substituting decoherence and amplitude damping for the general modifications of the electronic density matrix (Eqs. (55)–(57) and (66)), as discussed above.

IV. DISCUSSION

In this article, we have connected John Tully's FSSH algorithm to the QCLE of Kapral[33,34] and Martens.[31,32] To achieve this goal, we have constructed the equation of motion for the FSSH full nuclear-electronic density matrix and then applied a host of assumptions to reach the QCLE. In a sense, our perspective has been the polar opposite to the approach taken by Grunwald, Kim, and Kapral in Refs. 60 and 61. In those references, the authors began with the QCLE, chose a set of important quantum modes to generate a projected non-Markovian master equation in a subsystem basis, made a Markovian approximation in the kernel, and then lifted the resulting equation to a Markovian master equation in the full phase space. A detailed comparison between the two approaches is difficult to achieve for two reasons: (1) We invoke a unique trajectory approximation which has no clear analogue in the Grunwald approach; (2) Grunwald *et al.*[61] generated a master equation for propagating the electronic populations alone (i.e., the diagonal elements of the density matrix), whereas Tully-style surface hopping propagates extra degrees of freedom beyond the electronic populations (i.e., the amplitudes for each trajectory that offer information about coherence). As such, the Tully algorithm (i) can calculate expectation values for any electronic operator and (ii) finds hopping rates that can be calculated on-the-fly; by contrast, the Grunwald approach can calculate expectation values only for operators in the adiabatic electronic basis, and the hopping rates can be calculated only *post facto*. Despite these difficulties, future cross-comparisons would be extremely interesting.

For now, we believe our work justifies Tully's choices of walking along adiabats, momentum rescaling in the direction of the derivative coupling, and his particular choice of hopping rate. Nevertheless, as mentioned, this endorsement comes along only with several major (and some minor) assumptions, which should be discussed.

A. Unique trajectory assumption

Our approach suggests that FSSH dynamics cannot recover recoherences, which would correspond to multiple trajectories reaching the same point in phase space on the same surface.[34] Luckily, for many experiments, long-time decay rates and branching ratios are more important than the details of early recoherences. For modeling spectroscopy, though, this may well limit the applicability of FSSH-like algorithms. At the same time, it is worth emphasizing that the equation of motion for the Ehrenfest nuclear-electron density matrix does not satisfy the QCLE differential equation,[62] and one would thus expect Ehrenfest dynamics to be less accurate than FSSH where the QCLE is accurate.

B. Large velocity assumption

This paper confirms the common knowledge that FSSH will perform best when nuclei are moving quickly. Indeed, in his original paper, Tully[1] found that he could recover the Stuckelberg oscillations very well only at high velocity. At low velocities, FSSH does not do very well on Tully's second model problem.[1] That being said, the large velocity ($|\vec{P} \cdot \hat{d}| \gg |\Delta P|$) assumption may not be as severe as one would fear. After all, this assumption is invoked when we make a Taylor series for $\sigma(\vec{P} + \Delta P \hat{d}_{12})$ and then multiply by derivative coupling. Luckily, in regions of strong derivative coupling (for instance, an avoided crossing), ΔE is small which implies ΔP will be small. Thus, even though $|\vec{P} \cdot \hat{d}| \gg |\Delta P|$ cannot be true everywhere in phase space, the large velocity assumption may actually be quite good for many FSSH trajectories. Note that, in this paper, we have not discussed forbidden hops at all.

C. Modified electronic density matrix equation of motion

From a theoretical perspective, the most exciting result of this paper is that the equation of motion for the electronic density matrix (Eq. (9)) in FSSH can be altered to recover QCLE dynamics approximately. In particular, it is worth noting that according to Kapral's momentum-jump solution to the QCLE differential equation, one propagates some trajectories along surface 1 (with forces $\vec{F}_{11}$), some on surface 2 (with forces $\vec{F}_{22}$), and some on the equal-average surface (with forces $\frac{1}{2}(\vec{F}_{11} + \vec{F}_{22})$) – the latter option corresponding to an off-diagonal electronic density matrix element. It is quite interesting that we now have a new perspective for understanding this curious equal-average force: from the FSSH perspective, this equal-average force is recovered (at least partially) by decohering the off-diagonal density matrix with a rate proportional to $\frac{1}{2}(\vec{F}_{22} - \vec{F}_{11})$. See Eqs. (4), (53), and (55) above.

As a side note, there have been suggestions in the literature that a decoherence time scale for a given trajectory may be estimated by the potential energy difference over hbar ($\Delta V/\hbar$).[19,20,49,63] This article shows convincingly that this is not the best functional form for decoherence; decoherence rates between wave packets on different adiabatic surfaces must be proportional to the difference in forces.[12,13,21,26,52,64,65]

D. Minor assumptions

Going forward, it will be crucial to test all of the assumptions and conditions (major and minor) laid out in Sec. III. In Table I, we present a list of all the major and minor assumptions we have invoked in this paper to connect FSSH to the QCLE.

When are these conditions met? Layered comparisons between QCLE and FSSH dynamics will be very important for benchmarking and fully interpreting the practical limitations of the FSSH algorithm.

E. Immediate future goals

In practice, one immediate consequence of this article is a novel and very clear interpretation of the surface-hopping al-
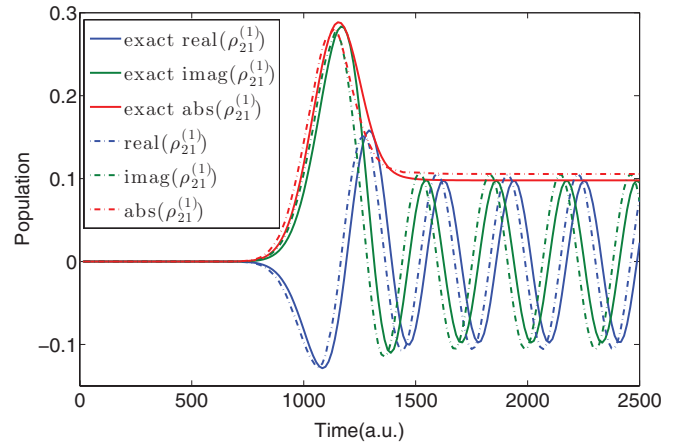

FIG. 1. The off-diagonal reduced electronic density matrix element for Tully's model problem #1 using the distribution $A_{21}^{(1)}$, i.e., $\rho_{21}^{(1)}(t) = \int dR \, dP \, A_{21}^{(1)}(R, P, t)$. We recover the exact result, at least qualitatively.

gorithm, including how to construct the partial Wigner transform in Eqs. (21), (31), and (32). Thus, we now have a much stronger sense of how to manipulate FSSH trajectories and evaluate arbitrary expectation values. For instance, there has been a long-standing problem in FSSH studies regarding how one should (if possible) transform between an adiabatic and diabatic basis, to evaluate diabatic populations.[66,67] We have just submitted a communication that resolves this FSSH problem.

Another question that can be addressed is the formal extension of FSSH to more than two electronic surfaces. Our preliminary analysis suggests that this can be done in a straightforward manner, and the general form of the consistency equations will be

$$\frac{\sigma_{jk}^{(i)}}{\sigma_{ii}^{(i)}} A_{ii} = \frac{\sigma_{jk}^{(k)}}{\sigma_{kk}^{(k)}} A_{kk} \tag{80}$$

and the equations of motion for the electronic density matrices must be altered appropriately.

A third question we are currently addressing is the validity of the equality $A_{21}^{(1)} = A_{21}^{(2)}$. To that end, in Figs. 1 and 2, we have plotted (as a function of time) the functions $\int dR \, dP \, A_{21}^{(1)}(t, R, P)$ and $\int dR \, dP \, A_{21}^{(2)}(t, R, P)$. These functions represent the off-diagonal element of the reduced electronic density matrix. The model problem is Tully's simple avoided crossing example (Tully problem #1 in Ref. 1). For comparison, we also plot the exact result $\int dR \langle \Phi_2(R) | \Psi(R, t) \rangle \langle \Psi(R, t) | \Phi_1(R) \rangle$.

Our initial wavefunction at the $t = 0$ is

$$\Psi(R, t = 0) = \sqrt{\frac{\pi}{w_0}} \exp\left(\frac{-(R - R_0)^2}{2w_0^2} + i k_0 R\right) |\Phi_1(R)\rangle, \tag{81}$$

where $k_0 = 18$, $w_0 = 1$, and $R_0 = -10$.

In theory, this model problem should be an easy application for FSSH because there is no need for a decoherence correction. Indeed, we find that FSSH can recover an off-diagonal matrix element quite well; both $A_{21}^{(1)}(t)$ and $A_{21}^{(2)}(t)$, are close to the exact result. In fact, a brute force average
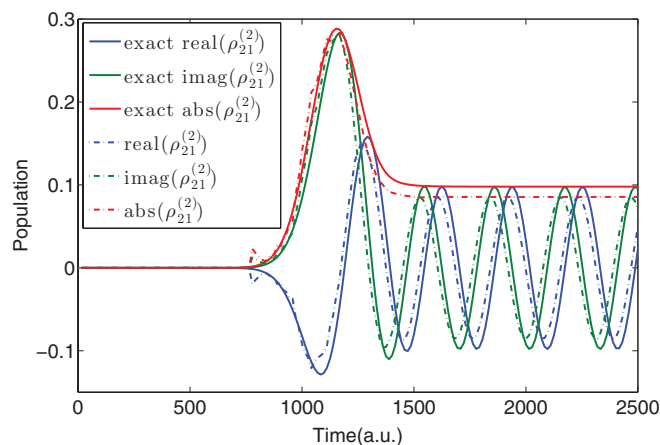
FIG. 2. The off-diagonal reduced electronic density matrix element for Tully's model problem #1 using the distribution $A_{21}^{(2)}$, i.e., $\rho_{21}^{(2)}(t)$ $= \int dR\,dP\,A_{21}^{(2)}(R, P, t)$. As before, we recover the exact result, at least qualitatively, thus demonstrating that our results do not depend strongly on which sampling function we use. There is slightly more noise in this plot compared with Fig. 1 because the particle starts on surface 1, so the statistics are not robust for early times.

of $\langle \sigma_{21} \rangle$ is also quite accurate here (not shown). One of our immediate goals is to investigate the accuracy of FSSH off-diagonal density matrix elements in great depth.

V. CONCLUSION AND FUTURE OUTLOOK

Using a host of assumptions, we have drawn a connection between a decoherence-modified version of Tully's FSSH algorithm and the Martens/Kapral QCLE. In so doing, we have given a proper and derivable framework for interpreting FSSH trajectories, so that we can recover the full density matrix (not just electronic populations). Thus, in the future, wherever surface-hopping is applicable, we now have the tools to calculate most observable properties. We should emphasize that our proposed FSSH nuclear-electronic density matrix **A** (Eqs. (21), (31), and (32)) has some attractive features:

- $\mathbf{A}(\vec{R}, \vec{P})$ is strictly Hermitian.
- $\int d\vec{R} \int d\vec{P}\,\mathrm{Tr}(\mathbf{A}(\vec{R}, \vec{P})) = 1$.
- We have some guaranteed positivity (in so much as $A_{11}(\vec{R}, \vec{P}, t)$, $A_{22}(\vec{R}, \vec{P}, t) \geq 0$). However, we are not guaranteed that $\begin{vmatrix} A_{11}(\vec{R}, \vec{P}, t) & A_{12}(\vec{R}, \vec{P}, t) \\ A_{21}(\vec{R}, \vec{P}, t) & A_{22}(\vec{R}, \vec{P}, t) \end{vmatrix} \geq 0$.

Of course, these positive attributes should be weighed against the necessary assumptions in Table I which must be tested. Finally, many new questions also arise from this paper including:

1. Can one say anything definitive about forbidden hops, which we have entirely ignored here?
2. Can the Shenvi phase correction (which gives empirically better results for one-dimensional recoherences[68,69]) be derived from this same approach?
3. Can we safely use independent trajectories to evaluate the decoherence rates in Eqs. (58) and (68) (rather than forcing all trajectories to communicate together)? If so, is A-FSSH[27,48] the most efficient way to implement an

approximate, independent trajectory, version of decoherence, or are better ways possible? At the same time, is it possible to implement interacting trajectories in an efficient and stable fashion?

4. The exact QCLE is not strictly invariant to time-translation for equilibrium time correlation functions;[70] what is the time-translational behavior of a corrected FSSH scheme?

Given the popularity of the FSSH algorithm, we expect that this swarm of questions will be stimulating for the field of quantum dynamics.

APPENDIX: IMPLEMENTATION OF A-FSSH

For completeness, we now fill in the missing details of the A-FSSH scheme. To evaluate Eqs. (75) and (76), one requires widths a_{R^α} for the distribution, which should properly be calculated at every time step and depend on the initial structure of the Wigner wave packet in phase space. For the A-FSSH algorithm,[27,48] one calculates a width by maximizing the overlap of $\langle g_1 | g_2 \rangle$, and thus estimates an effectively minimal rate of decoherence. The width then has the following quasi-variational form:

$$a_{R^\alpha}^2 = \hbar \frac{|R_1^\alpha - R_2^\alpha|}{|P_1^\alpha - P_2^\alpha|}. \tag{A1}$$

One estimates $\vec{R}_1 - \vec{R}_2$ and $\vec{P}_1 - \vec{P}_2$ from the $\Delta\vec{R}$ and $\Delta\vec{P}$ moments in Ref. 27. The final decoherence rate in A-FSSH is then

$$\frac{1}{\tau} \approx \frac{1}{2\hbar}\left(R_1^\alpha - R_2^\alpha\right)\left(F_1^\alpha - F_2^\alpha\right). \tag{A2}$$

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