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ABSTRACT

We investigate different approaches to derive the proper Floquet-based quantum–classical Liouville equation (F-QCLE) for laser-driven electron-nuclear dynamics. The first approach projects the operator form of the standard QCLE onto the diabatic Floquet basis and then transforms to the adiabatic representation. The second approach directly projects the QCLE onto the Floquet adiabatic basis. Both approaches yield a form that is similar to the usual QCLE with two modifications: (1) The electronic degrees of freedom are expanded to infinite dimension and (2) the nuclear motion follows Floquet quasi-energy surfaces. However, the second approach includes an additional cross derivative force due to the dual dependence on time and nuclear motion of the Floquet adiabatic states. Our analysis and numerical tests indicate that this cross derivative force is a fictitious artifact, suggesting that one cannot safely exchange the order of Floquet state projection with adiabatic transformation. Our results are in accord with similar findings by Izmaylov *et al.*, [J. Chem. Phys. 140, 084104 (2014)] who found that transforming to the adiabatic representation must always be the last operation applied, although now we have extended this result to a time-dependent Hamiltonian. This paper and the proper derivation of the F-QCLE should lay the basis for further improvements of Floquet surface hopping.

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I. INTRODUCTION

A computational understanding of light–matter interactions for a molecular system in a laser field is useful key for interpreting spectroscopy and photochemistry, where the dynamical interplay between electronic non-adiabatic transitions and photon excitation plays an important role in many exciting phenomena, such as molecular photodissociation[1–4] and coherent x-ray diffraction.[5–8] These phenomena usually involve dynamical processes in which electrons in a molecular system can make a transition through either (a) non-adiabatic coupling associated with the reorganization of nuclear configurations or (b) radiative coupling in conjunction with absorption or emission of photons. Thus, simulating these processes concurrently requires accurate theoretical treatments of both non-adiabatic molecular dynamics and light–matter interactions.[9–11] Over the past decades, many successful simulation schemes have been developed based on mixed quantum–classical frameworks in which the electronic wavefunction evolves according to quantum mechanics, while the nuclear degrees of freedom and the laser excitation are treated as classical parameters in a time-dependent electronic Hamiltonian.[12–18]

Among the myriad of semiclassical dynamics, Floquet-based fewest switch surface hopping (F-FSSH) has emerged as one of the most powerful methods, especially for simulating photodissociation and ionization in a monochromatic laser field.[19–21] In a nutshell, F-FSSH integrates Floquet theory with Tully's FSSH algorithm.[22] The general idea is to expand the electronic wavefunction in a

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Floquet state basis (with the electronic states dressed by $e^{im\omega t}$ for an integer m and the laser frequency ω) so that one can recast an explicitly time-dependent Hamiltonian into a time-independent Floquet Hamiltonian, albeit of infinite dimension. With the Floquet Hamiltonian, one can simply employ Tully's FSSH method in the Floquet state representation with a minimal modification.[19,20] In addition to the standard advantages of the usual surface hopping algorithm—stability, efficiency, and ease of incorporation with electronic structure calculations—F-FSSH also yields a better estimate for both the electronic and nuclear observables than other FSSH-based methods relying on instantaneous adiabatic surfaces.[12] Furthermore, given the time-independent nature of the Floquet Hamiltonian, many techniques designed to improve the standard FSSH method, such as velocity reversal and decoherence,[23–30] should be applicable within the Floquet formalism. That being said, due to the fact that one cannot directly derive Tully's FSSH—but rather only indirectly connect the equations of motion for FSSH dynamics with the quantum–classical Liouville equation (QCLE) in the adiabatic basis[31,32]—a proper understanding of the correct F-QCLE is crucial if we aim to make future progress in semiclassical modeling of light–matter interactions. Moreover, since it is well known that (1) FSSH performs best in an adiabatic (rather than diabatic) basis[22,33] and (2) FSSH can be connected to the QCLE only in an adiabatic basis,[31,32] we emphasize that for the sake of future progress, we require a proper understanding of the F-QCLE *in an adiabatic basis*.

Unfortunately, even without a light field, the proper derivation of the correct QCLE in an adiabatic basis is tricky—one can find two different versions of the QCLE if one invokes slightly different formal derivations. Following Kapral's approach,[34,35] the proper derivation of the standard QCLE includes two operations: (i) Wigner transformation and (ii) projection onto the adiabatic electronic state basis. First, one performs a partial Wigner transformation with respect to the nuclear degrees of freedom to obtain the operator form of the QCLE. Wigner transformation provides an exact framework to interpret the full quantum density matrix in terms of the joint electronic-nuclear probability density in the phase space of the nuclear configuration while retaining the quantum operator character of the electronic subsystem. Second, one projects the operator form of the QCLE onto the adiabatic electronic state basis obtained by diagonalizing the electronic Hamiltonian. This adiabatic representation allows the connection to electronic structure calculations in a mixed quantum–classical sense.[36–40] This approach is called the Wigner-then-Adiabatic (WA) approach. As Ryabinkin and co-workers have shown,[41] however, exchanging these two operations [the Adiabatic-then-Wigner (AW) approach] leads to a different QCLE that cannot capture geometric phase effects arising from a conical intersection (even though short time dynamics can sometimes be accurate[42,43]).

With this background in mind, the proper derivation of the F-QCLE is now even more challenging. In addition to the two operations above, there is a third step: one needs to dress the electronic states and expand the density matrix in the Floquet state basis. In the literature to date, the F-QCLE has been derived via the AW approach (projecting in the Floquet adiabatic representation and then performing partial Wigner transformation).[21] Nevertheless, as shown by Izmaylov and co-workers,[35,41] even in the limit of a time-independent Hamiltonian, such an (incorrect) AW approach will lead to a QCLE that neglects geometric phase related features in the nuclear dynamics or introduces artificial nuclear effects. Despite recent progress, the proper derivation of the F-QCLE is still an open question.

In this paper, our goal is to explore different approaches to derive the F-QCLE as we shuffle the three key operations and quantify their differences in the context of driven electron-nuclear dynamics. By isolating the correct F-QCLE, our work will not only validate F-FSSH methods but also provide means to improve surface hopping methods. This paper is organized as follows. In Sec. II, we formulate the three operations that are required to derive the F-QCLE. In Sec. III, we derive F-QCLEs via approaches with different orderings of operations. In Sec. IV, we implement F-FSSH calculations corresponding to these F-QCLEs and analyze their results for a modified avoided crossing model. We conclude with an outlook for the future in Sec. V.

For notation, we denote a quantum operator by $\hat{H}$ and use bold font for matrix $\mathbf{H}$. We use $\widetilde{\boldsymbol{H}}$ to denote the corresponding matrix in the expanded Floquet basis (infinite dimensional). The nuclear position and momentum are $\vec{R} = \{R^\alpha\}$ and $\vec{P} = \{P^\alpha\}$, respectively, where α is the nuclear coordinate index. We use a shorthand notation for the dot product: $X^\alpha \cdot Y^\alpha = \sum_\alpha X^\alpha Y^\alpha$.

II. THREE OPERATIONS

In the context of driven electron-nuclear dynamics, let us formulate the three necessary operations for deriving the F-QCLE. For a coupled electron-nuclei system driven by an external field of frequency ω, the total Hamiltonian takes the form of $\hat{H} = \hat{T}(\hat{P}^\alpha) + \hat{V}(\hat{R}^\alpha, t)$, where $\hat{T}(\hat{P}^\alpha) = \sum_\alpha \frac{(\hat{P}^\alpha)^2}{2M^\alpha}$ is the nuclear kinetic energy and $\hat{V}(\hat{R}^\alpha, t)$ is the electronic Hamiltonian with explicit time periodicity $\hat{V}(t) = \hat{V}(t+\tau)$ with $\tau = 2\pi/\omega$. Formally, the dynamics of the total system can be described by the time-dependent Schrödinger equation (TDSE) $i\hbar\frac{\partial}{\partial t}|\Psi\rangle = \hat{H}|\Psi\rangle$ of the total wavefunction $|\Psi\rangle$ or the quantum Liouville equation (QLE) $\frac{\partial}{\partial t}\hat{\rho} = -\frac{i}{\hbar}[\hat{H}, \hat{\rho}]$ of the total density matrix $\hat{\rho} = |\Psi\rangle\langle\Psi|$. To derive the F-QCLE, we need to apply the following three operations to the QLE.

A. Partial Wigner transformation of the nuclear degrees of freedom

To describe the dynamics in a mixed quantum–classical sense, we will follow Kapral's approach and perform a partial Wigner transformation with respect to the nuclear degrees of freedom,

$$\hat{\rho}_W(\vec{R}, \vec{P}, t) = \frac{1}{(2\pi\hbar)^N}\int d\vec{S}\left\langle \vec{R} + \frac{\vec{S}}{2}\middle|\hat{\rho}(t)\middle|\vec{R} - \frac{\vec{S}}{2}\right\rangle e^{-i\vec{P}\cdot\vec{S}/\hbar}, \quad (1)$$

where N is the dimension of the nuclear coordinate. A nuclear position eigenstate is defined as $\hat{R}^\alpha|R^\alpha\rangle = R^\alpha|R^\alpha\rangle$. In Eq. (1), the density matrix operator has been transformed into a Wigner wavepacket in phase space with coordinates $(\vec{R}, \vec{P})$. In what follows, we will denote the partial Wigner transformed operator by the subscript W [for example, $\hat{V}(\hat{R}^\alpha, t) \to \hat{V}_W(R^\alpha, t)$]. Note that after the partial Wigner transformation, $\hat{\rho}_W$ and $\hat{V}_W$ remain as electronic operators, while R^α and P^α are parameters.

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The equation of motion of the Wigner wavepacket can be obtained by transforming the QLE by $\frac{\partial}{\partial t}\hat{\rho}_W = -\frac{i}{\hbar}[(\hat{H}\hat{\rho})_W - (\hat{\rho}\hat{H})_W]$. The Wigner transform of operator products can further be expanded by the Wigner–Moyal operator $(\hat{H}\hat{\rho})_W = \hat{H}_W e^{-i\hbar\overleftrightarrow{\Lambda}/2}\hat{\rho}_W$ with $\overleftrightarrow{\Lambda} = \sum_\alpha \frac{\overleftarrow{\partial}}{\partial P^\alpha}\frac{\overrightarrow{\partial}}{\partial R^\alpha} - \frac{\overleftarrow{\partial}}{\partial R^\alpha}\frac{\overrightarrow{\partial}}{\partial P^\alpha}$.[35] Then, if we expand the Wigner–Moyal operator in Taylor series and truncate to the first order of $\hbar$, we obtain the operator form of the QCLE,

$$\frac{\partial}{\partial t}\hat{\rho}_W = -\frac{i}{\hbar}\left[\hat{V}_W, \hat{\rho}_W\right] - \frac{P^\alpha}{M^\alpha}\frac{\partial \hat{\rho}_W}{\partial R^\alpha} + \frac{1}{2}\left\{\frac{\partial \hat{V}_W}{\partial R^\alpha}, \frac{\partial \hat{\rho}_W}{\partial P^\alpha}\right\}. \tag{2}$$

Here, the commutator is $\left[\hat{A}, \hat{B}\right] = \hat{A}\hat{B} - \hat{B}\hat{A}$ and the anti-commutator is $\left\{\hat{A}, \hat{B}\right\} = \hat{A}\hat{B} + \hat{B}\hat{A}$. Note that Eq. (2) is exact if the partial Wigner transformed Hamiltonian is quadratic in R^α, for example, harmonic oscillators.

To propagate the Wigner wavepacket in Eq. (2), one must project the operator form of the QCLE in an electronic basis. One straightforward choice is to use a complete set of diabatic states for the electronic subsystem $\{|\mu\rangle\}$; such a set does not depend on any nuclear configuration. With this electronic diabatic basis, one can derive equations of motion for the density matrix ($A^{\text{dia}}_{\nu\mu} = \langle\nu|\hat{\rho}_W|\mu\rangle$) using matrix elements of the electronic Hamiltonian, $V_{\nu\mu}(\vec{R}, t) = \langle\nu|\hat{V}_W(\vec{R}, t)|\mu\rangle$. However, for many realistic electron–nuclei systems (and, certainly, any *ab initio* calculations), this diabatic QCLE cannot be solved since finding a complete set of exactly diabatic electronic states over a large set of nuclear geometries is rigorously impossible and quite demanding in practice even for approximate diabats.

B. Dress the electronic basis in the Floquet formalism

Let us now focus on the Floquet formalism, according to which one solves the TDSE by transforming the time-dependent Hamiltonian into a time-independent Floquet Hamiltonian in an extended Hilbert space of infinite dimension. For a moment, let us ignore all nuclear motion and focus on the electronic subsystem exclusively. According to Floquet theory, we utilize the time periodicity of the electronic Hamiltonian and dress the electronic diabatic states $\{|\mu\rangle\}$ by a time-periodic function $e^{im\omega t}$, where m is an integer formally from $-\infty$ to ∞. We denote the dressed state as the *Floquet diabatic state* $|\mu m\rangle \equiv e^{im\omega t}|\mu\rangle$. In terms of the Floquet diabatic basis, a time-periodic electronic wavefunction can be expressed as $|\Psi\rangle = \sum_{\mu m}\tilde{c}_{\mu m}|\mu m\rangle$, where $\tilde{c}_{\mu m}$ is an infinite dimensional state vector. The electronic wavefunction coefficient must satisfy the electronic TDSE,

$$i\hbar\sum_{\mu m}\frac{\partial \tilde{c}_{\mu m}}{\partial t}|\mu m\rangle = \sum_{\mu m}\hat{V}^{\text{F}}(t)|\mu m\rangle\tilde{c}_{\mu m}, \tag{3}$$

where the Floquet Hamiltonian operator is defined as

$$\hat{V}^{\text{F}}(t) \equiv \hat{V}(t) - i\hbar\frac{\partial}{\partial t}. \tag{4}$$

Next, we close Eq. (3) by multiplying both sides by $\langle\nu|$ and write $\langle\nu|\hat{V}^{\text{F}}(t)|\mu m\rangle = \sum_n \widetilde{V}^{\text{F}}_{\nu n,\mu m}e^{in\omega t}$ as a Fourier series,

$$i\hbar\sum_m\frac{\partial \tilde{c}_{\nu m}}{\partial t}e^{im\omega t} = \sum_{\mu m}\sum_n \widetilde{V}^{\text{F}}_{\nu n,\mu m}e^{in\omega t}\tilde{c}_{\mu m}. \tag{5}$$

Thus, the TDSE in Eq. (3) can be solved by grouping together all terms with the same time dependence, leading to the equation of motion for $\tilde{c}$,

$$i\hbar\frac{\partial}{\partial t}\tilde{c}_{\nu n} = \sum_{\mu m}\widetilde{V}^{\text{F}}_{\nu n,\mu m}\tilde{c}_{\mu m}. \tag{6}$$

The matrix elements of the Floquet Hamiltonian can be obtained by performing a Fourier transformation on the matrix elements,

$$\widetilde{V}^{\text{F}}_{\nu n,\mu m} = \langle\langle \nu n|\hat{V}^{\text{F}}|\mu m\rangle\rangle = \frac{1}{\tau}\int_0^\tau dt\langle\nu|\hat{V}^{\text{F}}(t)|\mu\rangle e^{i(m-n)\omega t}. \tag{7}$$

Here, we define the double bracket projection of an electronic operator by $\langle\langle \nu n|\cdots|\mu m\rangle\rangle = \frac{1}{\tau}\int_0^\tau dt\langle\nu|\cdots|\mu\rangle e^{i(m-n)\omega t}$. *Given that the electronic Hamiltonian operator $\hat{V}(t)$ is periodic in time, the double-bracket projection eliminates all time dependence*, and the Floquet Hamiltonian matrix reads

$$\widetilde{V}^{\text{F}}_{\nu n,\mu m} = \langle\langle \nu n|\hat{V}|\mu m\rangle\rangle + \delta_{\mu\nu}\delta_{mn}m\hbar\omega. \tag{8}$$

In the end, with this time-independent Hamiltonian, Eq. (6) can be formally solved by the exponential operator $\exp(-i\widetilde{\mathbf{V}}^{\text{F}}t/\hbar)$ with an arbitrary initial state.

At this point, we will allow nuclei to move and turn out attention to the equation of motion for the density matrix $\widehat{\rho}_W(\vec{R}, \vec{P}, t)$ within the Floquet diabatic basis. The Wigner-transformed density matrix in the Floquet diabatic representation is

$$\widetilde{A}^{\text{dia}}_{\nu n,\mu m}(\vec{R}, \vec{P}, t) = \langle\nu n|\widehat{\rho}_W(\vec{R}, \vec{P}, t)|\mu m\rangle. \tag{9}$$

For a proper F-QCLE, we will need to calculate the time derivative of $\widetilde{\mathbf{A}}^{\text{dia}}$,

$$\frac{\partial}{\partial t}\widetilde{A}^{\text{dia}}_{\nu n,\mu m} = \langle\nu n|\frac{\partial\widehat{\rho}_W}{\partial t}|\mu m\rangle - i(n-m)\hbar\omega\widetilde{A}^{\text{dia}}_{\nu n,\mu m}, \tag{10}$$

where the Floquet diabatic states depend on time explicitly. We begin by using Eq. (2) to project $\frac{\partial}{\partial t}\hat{\rho}_W$ into a Floquet diabatic basis. For the commutator term in Eq. (2), we can divide the operator product into matrix multiplication,

$$\begin{aligned}\langle\nu n|\left[\hat{V}_W, \hat{\rho}_W\right]|\mu m\rangle &= \sum_{\lambda l}\langle\langle \nu n|\hat{V}_W|\lambda l\rangle\rangle\widetilde{A}^{\text{dia}}_{\lambda l,\mu m} - \widetilde{A}^{\text{dia}}_{\nu n,\lambda l}\langle\langle \lambda l|\hat{V}_W|\mu m\rangle\rangle \\ &= \left[\widetilde{\mathbf{V}}_W, \widetilde{\mathbf{A}}^{\text{dia}}\right]_{\nu n,\mu m}.\end{aligned} \tag{11}$$

Here, we have inserted the identity of the diabatic electronic basis ($\hat{1} = \sum_\lambda|\lambda\rangle\langle\lambda|$), and expanded the time-dependent coefficients in terms of a Fourier series; see Appendix A for more details. Furthermore, if we combine Eq. (11) with the second term on the right-hand side of Eq. (10), we can write the sum of both terms as $[\widetilde{\mathbf{V}}^{\text{F}}, \widetilde{\mathbf{A}}^{\text{dia}}]$, i.e., we can replace $\widetilde{\mathbf{V}}_W$ with $\widetilde{\mathbf{V}}^{\text{F}}$.

For the anti-commutator term, we can use the same procedure to divide the operator product,

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$$\langle vn|\left\{\frac{\partial \hat{V}_W}{\partial R^\alpha}, \frac{\partial \hat{\rho}_W}{\partial P^\alpha}\right\}|\mu m\rangle = \sum_{\lambda l}\langle\langle vn|\frac{\partial \hat{V}_W}{\partial R^\alpha}|\lambda l\rangle\rangle \frac{\partial \widetilde{A}^{\rm dia}_{\lambda l,\mu m}}{\partial P^\alpha} + \frac{\partial \widetilde{A}^{\rm dia}_{vn,\lambda l}}{\partial P^\alpha}\langle\langle \lambda l|\frac{\partial \hat{V}_W}{\partial R^\alpha}|\mu m\rangle\rangle, \quad (12)$$

where $\langle vn|\frac{\partial \widehat{\rho}_W}{\partial P^\alpha}|\mu m\rangle = \frac{\partial}{\partial P^\alpha}\widetilde{A}^{\rm dia}_{vn,\mu m}$. Note that since the Floquet diabatic states do not depend on the nuclear coordinate, we can rewrite the derivative of the electronic Hamiltonian in terms of the Floquet Hamiltonian,

$$\langle\langle vn|\frac{\partial \hat{V}_W}{\partial R^\alpha}|\mu m\rangle\rangle = \frac{\partial}{\partial R^\alpha}\widetilde{V}^{\rm F}_{vn,\mu m}. \quad (13)$$

In the end, we may combine the above expressions to write down a complete *diabatic* F-QCLE,

$$\frac{\partial}{\partial t}\widetilde{\mathbf{A}}^{\rm dia} = -\frac{i}{\hbar}\left[\widetilde{\mathbf{V}}^{\rm F}, \widetilde{\mathbf{A}}^{\rm dia}\right] - \frac{P^\alpha}{M}\frac{\partial \widetilde{\mathbf{A}}^{\rm dia}}{\partial R^\alpha} + \frac{1}{2}\left\{\frac{\partial \widetilde{\mathbf{V}}^{\rm F}}{\partial R^\alpha}, \frac{\partial \widetilde{\mathbf{A}}^{\rm dia}}{\partial P^\alpha}\right\}. \quad (14)$$

As a final remark, we emphasize that the Floquet Hamiltonian $\widetilde{\mathbf{V}}^{\rm F} = \widetilde{\mathbf{V}}^{\rm F}(\vec{R})$ is a time-independent matrix, so Eq. (14) is simply the diabatic QCLE corresponding to an infinitely large electronic Hamiltonian $\widetilde{\mathbf{V}}^{\rm F}$.

C. Transformation to the adiabatic representation

To recast the diabatic F-QCLE in an adiabatic representation, we diagonalize the Floquet Hamiltonian matrix by solving the eigenvalue problem,

$$\sum_{vn}\widetilde{V}^{\rm F}_{\mu m,vn}(\vec{R})G^J_{vn}(\vec{R}) = \mathcal{E}^{\rm F}_J(\vec{R})G^J_{\mu m}(\vec{R}). \quad (15)$$

The eigenvalues $\mathcal{E}^{\rm F}_J = \mathcal{E}^{\rm F}_J(\vec{R})$ are the so-called Floquet quasi-energies with corresponding eigenvectors $G^J_{\mu m}(\vec{R})$. Since $\widetilde{\mathbf{V}}^{\rm F}$ is Hermitian, we can choose the eigenvectors $G^J_{\mu m}$ to be orthonormal so that we have the identities $\mathbf{G}^\dagger\mathbf{G} = \mathbf{G}\mathbf{G}^\dagger = \mathbf{I}$, i.e., $\sum_{\lambda\ell}G^{J*}_{\lambda\ell}G^K_{\lambda\ell} = \delta_{JK}$ and $\sum_L G^L_{\mu m}G^{L*}_{vn} = \delta_{\mu m,vn}$. The Floquet adiabatic state corresponding to the quasi-energy $\mathcal{E}^{\rm F}_J$ is

$$|\Phi^J(\vec{R},t)\rangle\rangle = \sum_{\mu m}G^J_{\mu m}(\vec{R})|\mu m\rangle. \quad (16)$$

As a practical matter, although $\widetilde{\mathbf{V}}^{\rm F}$ is infinite dimensional, we can truncate highly oscillating Floquet states by replacing $\sum_{m=-\infty}^{\infty}$ with $\sum_{m=-m_{\max}}^{m_{\max}}$.

With this Floquet adiabatic state basis, the probability density can be obtained by a diabatic-to-adiabatic transformation,

$$\widetilde{A}^{\rm adi}_{JK}(\vec{R},\vec{P},t) = \langle\Phi^J|\widehat{\rho}_W(\vec{R},\vec{P},t)|\Phi^K\rangle\rangle = \left(\mathbf{G}^\dagger\widetilde{\mathbf{A}}^{\rm dia}\mathbf{G}\right)_{JK}, \quad (17)$$

in the Floquet adiabatic representation. Note that since the eigenvectors $G^J_{\mu m}(\vec{R})$ do not depend on time explicitly, the time-derivative of the adiabatic probability density can be calculated simply to be

$$\frac{\partial \widetilde{\mathbf{A}}^{\rm adi}}{\partial t} = \mathbf{G}^\dagger\frac{\partial \widetilde{\mathbf{A}}^{\rm dia}}{\partial t}\mathbf{G}. \quad (18)$$

We are now ready to derive the adiabatic F-QCLE in Sec. III.

III. DIFFERENT APPROACHES TO DERIVE F-QCLE

In this section, we present several approaches with different orders for the three operations above; as will be shown, different orders will result in different adiabatic F-QCLEs. We summarize these approaches and the corresponding F-QCLEs in Table I.

A. Wigner-Floquet-Adiabatic (WFA) approach

Our first approach follows the order presented above: first we perform the partial Wigner transformation, second we project it to a Floquet diabatic basis, and third we transform it to an adiabatic representation. For the last step, following Eq. (18), we transform the diabatic F-QCLE by sandwiching the diabatic F-QCLE [Eq. (14)] with $\mathbf{G}^\dagger$ and $\mathbf{G}$. The first term on the right hand side of Eq. (14) (the commutator term) becomes

$$\sum_{vn}\sum_{\mu m}G^{J*}_{vn}\left[\widetilde{V}^{\rm F}, \widetilde{A}^{\rm dia}\right]_{vn,\mu m}G^K_{\mu m} = \left(\mathcal{E}^{\rm F}_J - \mathcal{E}^{\rm F}_K\right)\widetilde{A}^{\rm adi}_{JK}. \quad (19)$$

For the second term on the right hand side of Eq. (14), since the Floquet adiabatic states depend on the nuclear coordinate $\vec{R}$, the R^α derivative of the density must yield

$$\sum_{vn}\sum_{\mu m}G^{J*}_{vn}\frac{\partial \widetilde{A}^{\rm dia}_{vn,\mu m}}{\partial R^\alpha}G^K_{\mu m} = \frac{\partial \widetilde{A}^{\rm adi}_{JK}}{\partial R^\alpha} + \sum_L\left(D^\alpha_{JL}\widetilde{A}^{\rm adi}_{LK} - \widetilde{A}^{\rm adi}_{JL}D^\alpha_{LK}\right), \quad (20)$$

where the derivative coupling is

$$D^\alpha_{JK} = \langle\langle\Phi^J|\frac{\partial}{\partial R^\alpha}|\Phi^K\rangle\rangle = \sum_{\mu m}G^{J*}_{\mu m}\frac{\partial G^K_{\mu m}}{\partial R^\alpha}$$

corresponding to the change in the Floquet adiabatic states with respect to the nuclear coordinate R^α. Note that if the Floquet Hamiltonian is real-valued the diagonal element of the derivative coupling is zero ($D^\alpha_{JJ} = 0$). For the third term on the right hand side of Eq. (14) (the anti-commutator term), the R^α derivative of the Floquet Hamiltonian can be written in terms of the force matrix,

$$\sum_{vn}\sum_{\mu m}G^{J*}_{vn}\frac{\partial \widetilde{V}^{\rm F}_{vn,\mu m}}{\partial R^\alpha}G^K_{\mu m} = -F^\alpha_{JK}, \quad (21)$$

and explicitly,

$$F^\alpha_{JK} = -\frac{\partial \mathcal{E}^{\rm F}_J}{\partial R^\alpha}\delta_{JK} + \left(\mathcal{E}^{\rm F}_J - \mathcal{E}^{\rm F}_K\right)D^\alpha_{JK}.$$

The force matrix accounts for direct changes in the nuclear momentum associated with the electronic coupling. One can understand the diagonal element $F^\alpha_{JJ} = -\frac{\partial \mathcal{E}^{\rm F}_J}{\partial R^\alpha}$ as the classical force for nuclear

TABLE I. The F-QCLEs obtained via different approaches differ in the effective force matrices for nuclear motions.

F-QCLE		Effective force matrix
WFA	Equation (22)	$-\frac{\partial \mathcal{E}^{\rm F}_J}{\partial R^\alpha}\delta_{JK} + \left(\mathcal{E}^{\rm F}_J - \mathcal{E}^{\rm F}_K\right)D^\alpha_{JK}$
WAF	Equation (26)	$-\frac{\partial \mathcal{E}^{\rm F}_J}{\partial R^\alpha}\delta_{JK} + \left(\mathcal{E}^{\rm F}_J - \mathcal{E}^{\rm F}_K\right)D^\alpha_{JK} - \sum_{\mu m}m\hbar\omega G^{J*}_{\mu m}\frac{\partial G^K_{\mu m}}{\partial R^\alpha}$
AW	Equation (27)	$-\frac{\partial \mathcal{E}^{\rm F}_J}{\partial R^\alpha}\delta_{JK}$

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dynamics moving along the Jth Floquet quasi-energy surface in the phase space. The off-diagonal force term $F^{\alpha}_{JK} = (\mathcal{E}^{\mathrm{F}}_J - \mathcal{E}^{\mathrm{F}}_K)D^{\alpha}_{JK}$ for $J \neq K$ corresponds to nuclear velocity rescaling associated with non-adiabatic transitions between the Floquet quasi-energy surfaces.[34,35]

Finally, the F-QCLE via the WFA approach reads

$$\frac{\partial}{\partial t}\widetilde{A}^{\mathrm{adi}}_{JK} = -\frac{i}{\hbar}\left(\mathcal{E}^{\mathrm{F}}_J - \mathcal{E}^{\mathrm{F}}_K\right)\widetilde{A}^{\mathrm{adi}}_{JK} - \frac{P^{\alpha}}{M^{\alpha}}\frac{\partial \widetilde{A}^{\mathrm{adi}}_{JK}}{\partial R^{\alpha}} - \frac{P^{\alpha}}{M^{\alpha}}\sum_L\left(D^{\alpha}_{JL}\widetilde{A}^{\mathrm{adi}}_{LK} - \widetilde{A}^{\mathrm{adi}}_{JL}D^{\alpha}_{LK}\right) - \frac{1}{2}\sum_L\left(F^{\alpha}_{JL}\frac{\partial \widetilde{A}^{\mathrm{adi}}_{LK}}{\partial P^{\alpha}} + \frac{\partial \widetilde{A}^{\mathrm{adi}}_{JL}}{\partial P^{\alpha}}F^{\alpha}_{LK}\right). \tag{22}$$

We find that Eq. (22) takes exactly the same form as the standard QCLE in the adiabatic representation (for electron-nuclear dynamics without a driving laser).

B. Wigner-Adiabatic-Floquet (WAF) approach

For the second approach, we exchange the "adiabatic" and "Floquet" operations after the partial Wigner transformation. In this case, we directly project Eq. (2) onto the Floquet adiabatic basis $|\phi^J(\vec{R},t)\rangle\rangle$. Namely, we make the diabatic-to-adiabatic transformation of the Floquet electronic basis prior to the projection onto the dressed electronic states. Thus, we consider this path as the *Wigner-Adiabatic-Floquet* (WAF) approach.

Overall, we apply a procedure similar to what was used in Eq. (22). For the commutator term, we divide operator products using the same technique as in Appendix A. The R^{α} derivative term yields a derivative coupling term as the Floquet adiabatic basis depends on R^{α} explicitly. In the end, the WAF approach includes the first three terms exactly as Eq. (22). However, from the anti-commutator term of Eq. (2), the WAF approach leads to an additional cross derivative force. To see this, we focus on the derivative of the electronic Hamiltonian in the adiabatic representation,

$$\langle\langle \Phi^J|\frac{\partial \hat{V}}{\partial R^{\alpha}}|\Phi^K\rangle\rangle = \langle\langle \Phi^J|\frac{\partial \hat{V}^{\mathrm{F}}}{\partial R^{\alpha}}|\Phi^K\rangle\rangle + i\hbar\langle\langle \Phi^J|\frac{\partial}{\partial R^{\alpha}}\frac{\partial}{\partial t}|\Phi^K\rangle\rangle, \tag{23}$$

where we have used the definition of the Floquet Hamiltonian $\frac{\partial \hat{V}^{\mathrm{F}}}{\partial R^{\alpha}} = \frac{\partial \hat{V}}{\partial R^{\alpha}} - i\hbar\frac{\partial}{\partial R^{\alpha}}\frac{\partial}{\partial t}$. The derivative of the electronic Hamiltonian yields two terms: first, the same force matrix we obtained in Eq. (21),

$$\langle\langle \Phi^J|\frac{\partial \hat{V}^{\mathrm{F}}}{\partial R^{\alpha}}|\Phi^K\rangle\rangle = -F^{\alpha}_{JK}, \tag{24}$$

and second, a cross derivative force comes from the explicit dependence of the Floquet adiabatic states on both the nuclear coordinates and time,

$$i\hbar\langle\langle \Phi^J|\frac{\partial}{\partial R^{\alpha}}\frac{\partial}{\partial t}|\Phi^K\rangle\rangle = -\chi^{\alpha}_{JK},$$

and explicitly,

$$\chi^{\alpha}_{JK} = \sum_{\mu m} m\hbar\omega G^{J*}_{\mu m}\frac{\partial G^{K}_{\mu m}}{\partial R^{\alpha}}. \tag{25}$$

Note that unlike the derivative coupling D^{α}_{JK}, the diagonal element of χ^{α}_{JK} is non-zero and real-valued.

Finally, in the same Floquet adiabatic basis as given by Eq. (16), the F-QCLE reads

$$\frac{\partial}{\partial t}\widetilde{A}^{\mathrm{adi}}_{JK} = -\frac{i}{\hbar}\left(\mathcal{E}^{\mathrm{F}}_J - \mathcal{E}^{\mathrm{F}}_K\right)\widetilde{A}^{\mathrm{adi}}_{JK} - \frac{P^{\alpha}}{M^{\alpha}}\frac{\partial \widetilde{A}^{\mathrm{adi}}_{JK}}{\partial R^{\alpha}} - \frac{P^{\alpha}}{M^{\alpha}}\sum_L\left(D^{\alpha}_{JL}\widetilde{A}^{\mathrm{adi}}_{LK} - \widetilde{A}^{\mathrm{adi}}_{JL}D^{\alpha}_{LK}\right) - \frac{1}{2}\sum_L\left(F^{\alpha}_{JL} + \chi^{\alpha *}_{LJ}\right)\frac{\partial \widetilde{A}^{\mathrm{adi}}_{LK}}{\partial P^{\alpha}} + \frac{\partial \widetilde{A}^{\mathrm{adi}}_{JL}}{\partial P^{\alpha}}\left(F^{\alpha}_{LK} + \chi^{\alpha}_{LK}\right). \tag{26}$$

We observe that while Eqs. (22) and (26) take the same form, the "effective" force matrix (defined as the coefficients of $\frac{\partial \widetilde{\mathbf{A}}^{\mathrm{adi}}}{\partial P^{\alpha}}$) includes an additional cross derivative force that indicates the difference between these two equations. In other words, even though these two QCLEs will propagate electrons equivalently, the difference in the "effective" force matrix will lead to different nuclear dynamics in phase space. Specifically, from Eq. (26), the classical force on the Jth quasi-energy surface is given by $F^{\alpha}_{JJ} + \chi^{\alpha}_{JJ}$, implying that the nuclear dynamics should experience the additional cross derivative force on top of the Floquet quasi-energy surface.

C. Adiabatic-then-Wigner (AW) approach

Finally, for completeness, we should emphasize that the first derivation of an F-QCLE was published by Horenko, Schmidt, and Schütte, who used an approach that was different from either of the approaches above. In Ref. 21, these authors derived their F-QCLE using an Adiabatic-then-Wigner (AW) approach. Their final equation of motion is

$$\frac{\partial}{\partial t}\widetilde{A}^{\mathrm{adi}}_{JK} = -\frac{i}{\hbar}\left(\mathcal{E}^{\mathrm{F}}_J - \mathcal{E}^{\mathrm{F}}_K\right)\widetilde{A}^{\mathrm{adi}}_{JK} - \frac{P^{\alpha}}{M^{\alpha}}\frac{\partial \widetilde{A}^{\mathrm{adi}}_{JK}}{\partial R^{\alpha}} - \frac{P^{\alpha}}{M^{\alpha}}\sum_L\left(D^{\alpha}_{JL}\widetilde{A}^{\mathrm{adi}}_{LK} - \widetilde{A}^{\mathrm{adi}}_{JL}D^{\alpha}_{LK}\right) + \frac{1}{2}\sum_L\left(\frac{\partial \mathcal{E}^{\mathrm{F}}_J}{\partial R^{\alpha}} + \frac{\partial \mathcal{E}^{\mathrm{F}}_K}{\partial R^{\alpha}}\right)\frac{\partial \widetilde{A}^{\mathrm{adi}}_{JK}}{\partial P^{\alpha}}. \tag{27}$$

As mentioned above, in the limit of a time-independent Hamiltonian, Ryabinkin and co-workers have shown that the AW approach results in the loss of geometric phase related features for a 2D problem;[41] the WA approach is far more accurate (see figures in Ref. 41). Moreover, in contrast to Eqs. (22) and (26), the last term in Eq. (27) does not include any off-diagonal force term, which implies no momentum rescaling. Within a surface hopping context, a lack of momentum rescaling will inevitably lead to a violation of detailed balance.[44–46] Note that early numerical assessments of the AW approach did not investigate either geometric phase effects or detailed balance.[42,43] For these reasons, we expect the AW approach to the F-QCLE to be less accurate than the WFA and WAF approaches. Nevertheless, to satisfy the readers who are curious about the original AW approach, we will present the relevant transmission and reflection probabilities and final momentum distribution data in Appendix B, which should

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remind one why momentum jumps are so important for scattering calculations.[47]

IV. RESULTS

A. Shifted avoided crossing model

To analyze the difference between these approaches, we consider a shifted avoided crossing model composed of a two-level electronic system coupled to a 1D nuclear motion. The diabatic electronic states are denoted as $|g\rangle$ and $|e\rangle$, and the electronic Hamiltonian is given by

$$\hat{V}(R,t) = \begin{pmatrix} V_{gg}(R) & V_{ge}(R,t) \\ V_{eg}(R,t) & V_{ee}(R) \end{pmatrix}, \tag{28}$$

where the diabatic energy is given by

$$V_{gg}(R) = \begin{cases} A(1-e^{-BR}), & R>0 \\ -A(1-e^{BR}), & R<0, \end{cases} \tag{29}$$

$$V_{ee}(R) = -V_{gg}(R) + \hbar\omega, \tag{30}$$

and the diabatic coupling is periodic in time,

$$V_{ge}(R,t) = V_{eg}(R,t) = Ce^{-DR^2}\cos\omega t. \tag{31}$$

The parameters are $A = 0.01$, $B = 1.6$, $C = 0.01$, and $D = 1.0$, and the nuclear mass is $M = 2000$. Note that this model is Tully's simple avoided crossing model with two modifications: the diabatic coupling becomes time-periodic and the excited potential energy surface is shifted by $\hbar\omega$. For simplicity, we choose the laser frequency $\hbar\omega = 0.024$ large enough ($\hbar\omega > 2A$) so that the diabatic Floquet states $|gm\rangle$ have an avoided crossing only with $|e(m-1)\rangle$ (at $R = 0$) and do not have any trivial crossings. The size of the Floquet basis is truncated by $m_{\max} = 4$ as the laser field is weak ($C/\hbar\omega < 1$).

We assume that the initial wavepacket is Gaussian centered at the initial position R_0 and momentum P_0 on diabat $|g\rangle$,

$$|\Psi_0\rangle = \frac{1}{\mathcal{N}}\exp\left(-\frac{(R-R_0)^2}{2\sigma^2} + \frac{i}{\hbar}P_0(R-R_0)\right)|g\rangle, \tag{32}$$

where the normalization factor is $\mathcal{N}^4 = \pi\sigma^2$. The width of the Gaussian is chosen to be $\sigma = 20\hbar/P_0$. The wavepacket can be propagated exactly in the diabatic representation.

B. F-FSSH based on WFA and WAF

To show the difference between the dynamics as obtained by the different F-QCLEs, we will simulate F-FSSH results for both the WFA and WAF approaches. Within F-FSSH, we describe the propagation of the Floquet wavepacket by a swarm of trajectories, each with its own electronic amplitudes $\tilde{c}_J$ satisfying

$$\frac{\partial \tilde{c}_J}{\partial t} = -\frac{i}{\hbar}\mathcal{E}_J^{\mathrm{F}}\tilde{c}_J - \frac{P}{M}\sum_L D_{JL}\tilde{c}_L, \tag{33}$$

where $\mathcal{E}_J^{\mathrm{F}} = \mathcal{E}_J^{\mathrm{F}}(R)$, $D_{JL} = D_{JL}(R)$, $R = R(t)$, and $P = P(t)$ representing nuclear trajectory. All nuclear trajectories move classically along an active Floquet state (J) obeying

$$\frac{dR}{dt} = \frac{P}{M}, \tag{34}$$

$$\frac{dP}{dt} = \begin{cases} -\dfrac{\partial \mathcal{E}_J^{\mathrm{F}}}{\partial R} & \text{for WFA} \\ -\dfrac{\partial \mathcal{E}_J^{\mathrm{F}}}{\partial R} - \chi_{JJ} & \text{for WAF.} \end{cases} \tag{35}$$

Here, based on the connection between the QCLE and FSSH, the nuclear force in Eq. (35) is determined according to the diagonal element of the effective force matrix in the F-QCLEs.

Consistent with the standard FSSH technique, the hopping probability from active Floquet state J to state K is given by

$$\mathrm{Prob}(J\to K) = -2\mathrm{Re}\left(\frac{P^\alpha}{M^\alpha}\cdot D_{KJ}^\alpha\frac{\tilde{c}_J\tilde{c}_K^*}{|\tilde{c}_J|^2}\right)dt,$$

where dt is the classical time step. After each successful hop, the velocity is adjusted to conserve the total Floquet quasi-energy. If a frustrated hop occurs, we implement velocity reversal.[25] Note that we neglect the decoherence correction since the over-coherence problem should not be severe for a simple avoided crossing model.[48]

In the end, the probability to measure diabatic state μ can be evaluated by the density matrix interpretation,[49]

$$P_\mu = \sum_m \frac{N(\mu m)}{N_{\mathrm{traj}}} + \sum_{n\neq m}\frac{\sum_l^{N(\mu m)}\sum_k^{N(\mu n)}\tilde{c}_{\mu m}^{(l)}\tilde{c}_{\mu n}^{(k)*}e^{i(m-n)\omega t}}{N(\mu m)N(\mu n)}, \tag{36}$$

where $N(\mu m) = \sum_l^{N_{\mathrm{traj}}}\delta_{J^{(l)}\mu m}$ is the number of the trajectories that have the active surface $J^{(l)}$ end up on the Floquet state $|\mu m\rangle$. Here, l and k are the trajectory indices. We propagate N_{traj} trajectories for an amount of time long enough for each trajectory to pass through the coupling region ($|R| < 3$ for this parameter set).

C. Effective Floquet quasi-energy surfaces for nuclear dynamics

First, we analyze the effective potential energy surfaces for nuclear dynamics by integrating Eq. (35) over R for the WFA and WAF approaches, respectively. For the WFA approach, the effective PES simply recovers the Floquet quasi-energy surfaces $\mathcal{E}_J^{\mathrm{F}}$. For the WAF approach, the effective PES is obtained by $V_{eff}(R) = \mathcal{E}_J^{\mathrm{F}}(R) + \int_{-\infty}^{R}\chi_{JJ}(R')dR'$, where the quasi-energy surface is modified by the integration of the cross derivative force. We find that including the cross derivative force in the WAF approach increases the crossing barrier for the nuclear dynamics on the lower adiabat (see Fig. 1). Note that in terms of an F-FSSH calculation, these changes will have a direct effect on the nuclear dynamics, but not the electronic amplitudes.

D. Transmission and reflection

Next, we turn our attention to the transmission and reflection probabilities produced by the F-FSSH calculations. Overall, the WFA results are more accurate than the WAF results. In Fig. 2, we

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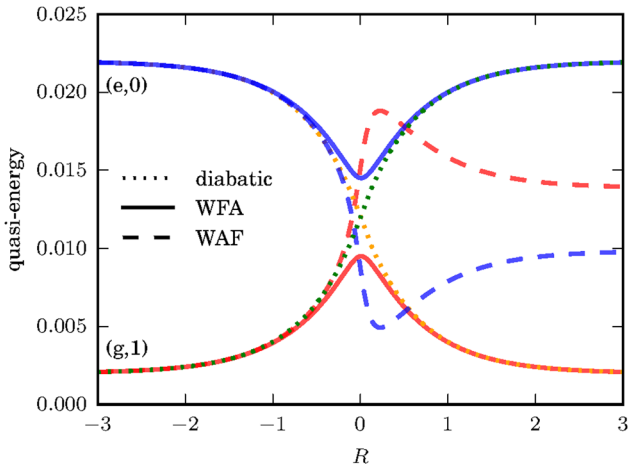


FIG. 1. The effective potential energy surfaces for the WFA approach (solid lines) and the WAF approach (dashed lines). The lower (upper) quasi-energy surface is in red (blue). The diabatic Floquet state energies $\widetilde{V}^{F}_{\mu m,\mu m}$ are plotted for $|g1\rangle$ (green) and $|e0\rangle$ (orange) in dotted lines. Note that the barrier height and the equilibrium energy ratio of the WAF surface are significantly modified (relative to the WFA approach) by the presence of the additional cross derivative force.

find that according to the WFA approach, there should be a rise in transmission on the lower adiabat around $P_0 \approx 5.3$, which is the momentum for which transmission should be allowed classically; see the barrier height (≈0.007) in Fig. 1. Indeed, such a threshold at $P_0 \approx 5.3$ is found according to the exact wavefunction simulation as well. However, for the WAF approach with the cross derivative force, one find a higher crossing barrier energy (≈0.015), and the transmission on the lower adiabat occurs (incorrectly) at $P_0 \approx 7.8$. This result suggests that the cross derivative force is a fictitious term: the WAF semiclassical derivation is spurious.

Let us now focus on the WFA results in more detail. Several points are worth mentioning. First, the transmission to the upper adiabat occurs after $P_0 \approx 8.9$, which agrees with the classical energy difference $2A = 0.02$ [see Eq. (29) for the definition of A]. Second, for high initial momentum ($P_0 > 8.0$), the F-FSSH-WFA can almost recover the correct nuclear dynamics. Third, in the intermediate momentum region $P_0 \in (6, 8)$, unfortunately, the F-FSSH wavepacket exhibits less transmission than the exact calculation. This discrepancy may be attributed to FSSH's inability to capture nuclear tunneling effects.

V. CONCLUSION AND OUTLOOK

We have analyzed three approaches for deriving the QCLE within a Floquet formalism and found three different F-QCLEs. While these F-QCLEs take similar forms, the difference in the effective force matrix can lead to large discrepancies in nuclear dynamics. As such, in the context of driven electron-nuclear dynamics, our results reiterate the fact that one cannot change the order of operations in the derivation of the correct QCLE. Specifically, as opposed to the WFA approach, the WAF approach [exchanging Floquet electronic basis dressing (F) and adiabatic transformation (A)] is spurious. Overall, our results are very consistent with the results of Izmaylov and Kapral,[41] who found that one must be careful when

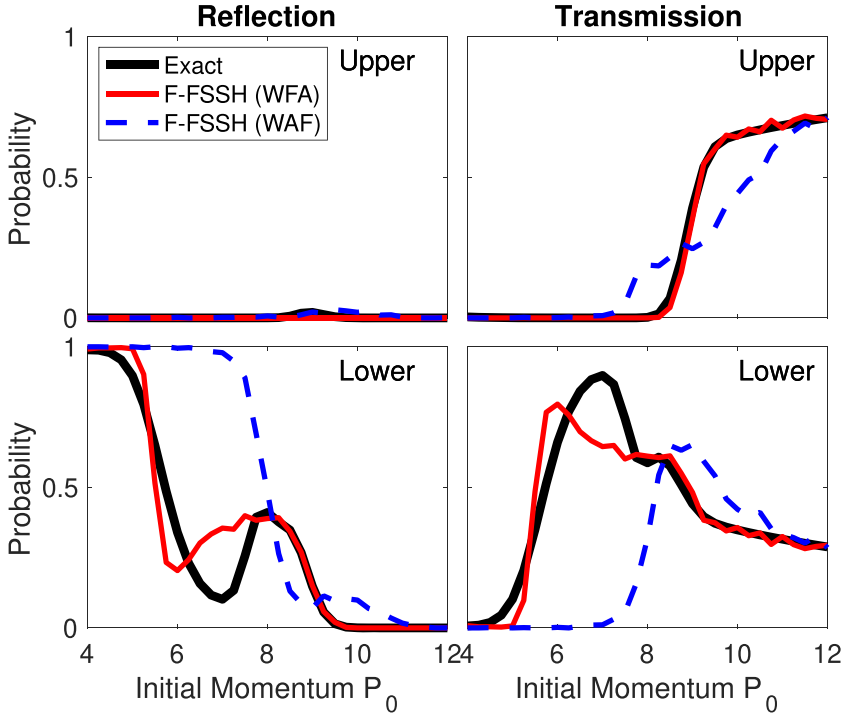


FIG. 2. The probability of transmission (right) and reflection (left) on the upper and lower adiabats as a function of the initial momentum. The F-FSSH dynamics is implemented using the effective nuclear forces of the WFA (red) and WAF (blue). Overall, the WFA result is more accurate than the WAF result. The WFA result almost recovers the correct nuclear dynamics. Due to the cross derivative force, the nuclear trajectory of the F-FSSH(WAF) experiences a much higher crossing barrier, requiring larger P_0 for transmission.

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deriving the QCLE even without time dependence; they have already shown that the AW approach does not include any geometric phase information. Thus, in the end, with or without a time-dependent Hamiltonian, it appears that, provided that one moves to the adiabatic representation as the very last step, one will always derive the correct semiclassical equation of motion.

Looking forward, the derivation of the F-QCLE presented here validates the F-FSSH method and paves the way for further improvements in the future. With regard to coherence and decoherence, given the time-independent nature of the Floquet Hamiltonian, we can immediately apply many decoherence schemes, including augmented moment decoherence,[28,48,50–52] to the F-FSSH algorithm. As far as the geometric phase effect is concerned, it is known that Berry phases are already included within the QCLE[53] for a time-independent electronic Hamiltonian, and so we would expect that similar effects should already be included within this proper F-QCLE for periodic (time-dependent) electronic Hamiltonians. However, there is one nuance that we have conveniently neglected in the present paper. Note that according to Eq. (7), we have every reason to believe that the F-QCLE formalism (especially for a non-monocrhomatic driving field with more than one Fourier mode in the time-dependent Hamiltonian) will necessarily introduce a complex (i.e., not real-valued) Floquet Hamiltonian. In such a case, we should find not just Berry phases but also Berry force.[54] Future research into the nature of this intrinsic magnetic Berry force—how or if it appears in the context of F-QCLE and surface hopping dynamics—is currently underway and represents an exciting new direction for non-adiabatic theory.

Finally, it has been recently reported that novel control schemes, such as Floquet engineering,[55,56] can enhance the excitation energy transfer rate even in the presence of strong fluctuations and dissipation. Given so many potential applications for F-QCLE simulations, we believe that the present study will find an immediate use in the physical chemistry and chemical physics community.

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APPENDIX A: REWRITING THE PRODUCT OF WIGNERIZED OPERATORS AS MATRIX MULTIPLICATION IN THE FLOQUET REPRESENTATION

Throughout this paper, we have constantly used one trick. Namely, we have consistently rewritten the product of two Wigner transformed operators (one of which must be time-periodic) into a non-standard matrix product in the Floquet representation. To see how this trick works in practice, we consider (for example) the operator product $\hat{\rho}_W \hat{H}_W$.

We insert the electronic identity operator $\hat{1} = \sum_\lambda |\lambda\rangle\langle\lambda|$ between $\hat{\rho}_W$ and $\hat{H}_W$,

$$\langle vn|\hat{\rho}_W \hat{H}_W|\mu m\rangle = \sum_\lambda \langle vn|\hat{\rho}_W|\lambda\rangle\langle\lambda|\hat{H}_W|\mu m\rangle. \tag{A1}$$

Next, as in Sec. II, we express $\langle\lambda|\hat{H}_W|\mu m\rangle$ in the form of a Fourier series,

$$\langle\lambda|\hat{H}_W|\mu m\rangle = \sum_l \langle\langle\lambda l|\hat{H}_W|\mu m\rangle\rangle e^{il\omega t}, \tag{A2}$$

where the double bracket projection is defined by the Fourier transform. With the Fourier series, we write $|\lambda\rangle e^{il\omega t} = |\lambda l\rangle$ and obtain

$$\langle vn|\hat{\rho}_W \hat{H}_W|\mu m\rangle = \sum_{\lambda l} \langle vn|\hat{\rho}_W|\lambda l\rangle\langle\langle\lambda l|\hat{H}_W|\mu m\rangle\rangle. \tag{A3}$$

APPENDIX B: THE AW APPROACH

Following Ref. 21, one can derive the F-QCLE through an AW approach by invoking the wavefunction ansatz $|\Psi(\vec{R},t)\rangle = \sum_J \tilde{a}_J(\vec{R},t)|\phi^J(\vec{R},t)\rangle$ in the Floquet adiabatic basis given by Eq. (16), and then, we insert this ansatz into the TDSE and obtain the equation of motion for $\tilde{a}_J(\vec{R},t)$ in the form of $i\hbar\frac{\partial}{\partial t}\tilde{a}_J = \sum_K \hat{H}^{\text{adi}}_{JK}\tilde{a}_K$. Here, the adiabatic Hamiltonian operator is given by

$$\hat{H}^{\text{adi}}_{JK} = \left(\mathcal{E}^{\text{F}}_J(R^\alpha) + \frac{(\hat{P}^\alpha)^2}{2M^\alpha}\right)\delta_{JK} - i\hbar D^\alpha_{JK}\cdot\frac{\hat{P}^\alpha}{M^\alpha} + O(\hbar^2), \tag{B1}$$

and the nuclear momentum operator is $\hat{P}^\alpha = -i\hbar\frac{\partial}{\partial R^\alpha}$. Thereafter, one writes the equation of motion for the density matrix ($\widetilde{A}^{\text{adi}}_{JK} = \tilde{a}_J\tilde{a}^*_K$) as $\frac{\partial}{\partial t}\widetilde{\mathbf{A}}^{\text{adi}} = -\frac{i}{\hbar}[\hat{\mathbf{H}}^{\text{adi}}, \widetilde{\mathbf{A}}^{\text{adi}}]$ and performs a partial Wigner transformation using the Wigner–Moyal operator,

$$\frac{\partial}{\partial t}\widetilde{\mathbf{A}}^{\text{adi}} = -\frac{i}{\hbar}\left(\widetilde{\mathbf{H}}^{\text{adi}}_W e^{-i\hbar\overleftrightarrow{\Lambda}/2}\widetilde{\mathbf{A}}^{\text{adi}} - \widetilde{\mathbf{A}}^{\text{adi}} e^{-i\hbar\overleftrightarrow{\Lambda}/2}\widetilde{\mathbf{H}}^{\text{adi}}_W\right). \tag{B2}$$

The Wigner transform of the adiabatic Hamiltonian operator reads

$$(\widetilde{H}^{\text{adi}}_W)_{JK} = \left(\mathcal{E}^{\text{F}}_J(R^\alpha) + \frac{(P^\alpha)^2}{2M^\alpha}\right)\delta_{JK} - i\hbar D^\alpha_{JK}\cdot\frac{P^\alpha}{M^\alpha}. \tag{B3}$$

Next, following the same procedure in Sec. II A, we expand the Wigner–Moyal operator and truncate the equation of motion to the first order of $\hbar$. In the end, we obtain Eq. (27), which is equivalent to Eq. (44) in Ref. 21 for the case of the monochromatic external field (i.e., $\frac{dF_0}{dt} = 0$ using the notation of Ref. 21).

In Fig. 3, we compare the F-FSSH results for the AW vs WFA F-QCLEs. Note that because of the absence of the off-diagonal force terms in Eq. (27), the corresponding AW F-FSSH trajectories neglect velocity rescaling when hopping between the Floquet adiabatic surfaces. Thus, an AW trajectory can hop to the upper adiabat (the blue adiabatic potential in Fig. 1) without worrying about energy conservation. Note that according to Fig. 3, the AW approach does outperform the WAF approach; see Fig. 2. However, the AW approach is far less accurate than the WFA approach. In particular, Fig. 3(a) shows that the AW approach overestimates the transmission probability on the upper adiabat (presumably because of the lack of velocity rescaling). Furthermore, Fig. 3(b) demonstrates that the

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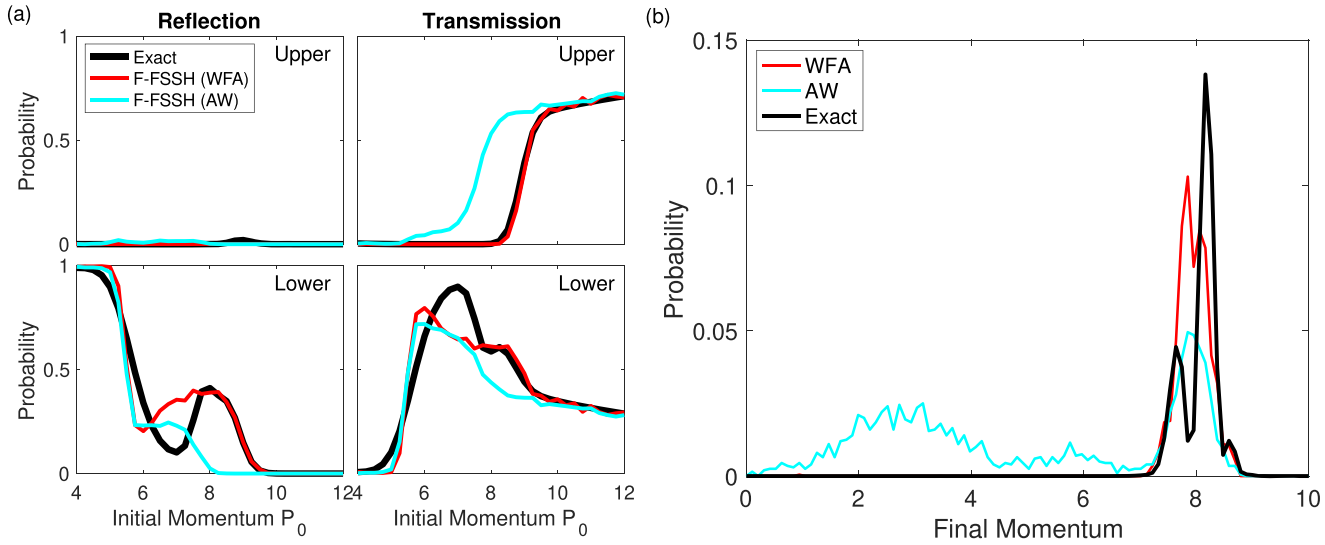


FIG. 3. (a) The transmission and reflection probabilities for the same scattering problem as in Fig. 2 and (b) the final momentum distribution (averaged over all channels) for incoming momentum $P_0 = 8$. Here, we calculate data using F-FSSH dynamics corresponding to the WFA (red) and AW (cyan) approaches, as well as the exact wavepacket propagation (black). The AW approach clearly leads to incorrect estimates of transmission and reflection in the region $6 \lesssim P_0 \lesssim 8$ due to the lack of velocity rescaling, as well as an incorrect momentum distribution, especially in the lower momentum region.

asymptotic velocities are also incorrect. Although these data necessarily rely on an F-FSSH implementation, altogether, Fig. 3 strongly suggests that the AW approach to the F-QCLE as given in Eq. (27) is not optimal—in agreement with the conclusions of Izmaylov *et al.*

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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