High-order geometric integrators for representation-free Ehrenfest dynamics

Seonghoon Choi and Jiří Vaníček

Laboratory of Theoretical Physical Chemistry, Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015, Lausanne, Switzerland

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Ehrenfest dynamics is a useful approximation for ab initio mixed quantum-classical molecular dynamics that can treat electronically nonadiabatic effects. Although a severe approximation to the exact solution of the molecular time-dependent Schrödinger equation, Ehrenfest dynamics is symplectic, time-reversible, and conserves exactly the total molecular energy as well as the norm of the electronic wavefunction. Here, we surpass apparent complications due to the coupling of classical nuclear and quantum electronic motions and present efficient geometric integrators for “representation-free” Ehrenfest dynamics, which do not rely on a diabatic or adiabatic representation of electronic states and are of arbitrary even orders of accuracy in the time step. These numerical integrators, obtained by symmetrically composing the second-order splitting method and exactly solving the kinetic and potential propagation steps, are norm-conserving, symplectic, and time-reversible regardless of the time step used. Using a nonadiabatic simulation in the region of a conical intersection as an example, we demonstrate that these integrators preserve the geometric properties exactly and, if highly accurate solutions are desired, can be even more efficient than the most popular non-geometric integrators.

a) Electronic mail: seonghoon.choi@epfl.ch
b) Electronic mail: jiri.vanicek@epfl.ch
I. INTRODUCTION

Mixed quantum-classical methods, such as the surface hopping, mean-field Ehrenfest dynamics, and methods based on the mixed quantum-classical Liouville equation or the Meyer–Miller–Stock–Thoss mapping Hamiltonian, remedy one of the shortcomings of classical molecular dynamics: its inability to describe electronically nonadiabatic processes involving significantly coupled states. Although a severe approximation to the exact quantum solution, Ehrenfest dynamics can provide a useful first picture of nonadiabatic dynamics in some, especially strongly coupled systems. Indeed, Ehrenfest dynamics was successfully used to describe electron transfer, nonadiabatic processes at metal surfaces, and photochemical processes. The mean-field theory was also employed to simplify the evaluation of the memory kernel in the generalized master equation formalism. In addition, Ehrenfest dynamics provides a starting point for various refined methods. For example, a multi-trajectory, locally mean-field generalization of Ehrenfest dynamics was used to evaluate vibronic spectra and, when combined with the semiclassical initial value representation, can describe even wavepacket splitting. A further generalization, the multiconfigurational Ehrenfest method, includes correlations between Ehrenfest trajectories. In what follows, we shall only consider the basic, mean-field Ehrenfest method, whose validity conditions were formulated by Bornemann et al.

The coupling between nuclear and electronic dynamics complicates the numerical integration in Ehrenfest dynamics. The widely-used two and three time step methods improve the efficiency by using different integration time steps that account for the different time scales of nuclear and electronic motions (see Appendix A). However, such integration schemes violate the geometric properties of the exact solution: the simpler, two time step method is irreversible and neither method is symplectic (see Fig. 6 in Appendix A). Almost every geometric property can, however, be preserved exactly by employing the symplectic integrators based on the splitting method. This splitting method is widely applicable—so long as the Hamiltonian can be decomposed into exactly solvable parts—and was employed to obtain symplectic integrators in many well-known applications, including molecular quantum and classical dynamics, Schrödinger–Liouville–Ehrenfest dynamics and the Meyer–Miller–Stock–Thoss mapping approach. In particular, because the Ehrenfest method in either the adiabatic or diabatic representation can be formu-
lated as a special case of the mapping method, the integrators developed for one of these two methods should also be applicable to the other. Motivated by on-the-fly \textit{ab initio} applications that employ increasingly practical real-time time-dependent electronic structure methods, here we present integrators that—in contrast to the integrators formulated in the mapping approach—do not rely on any particular representation of electronic states and thus avoid the expensive construction of a truncated diabatic or adiabatic electronic basis.

Typically, to reach the same accuracy, geometric integrators need greater computational effort than their non-geometric counterpart. Yet, the efficiency of geometric integrators can be improved significantly by employing various composition methods. Thus obtained integrators of high orders of convergence in the time step offer the best of both worlds: they are efficient while conserving the relevant geometric structure exactly.

After showing analytically, in Sec. \[ \text{II} \] that the high-order geometric integrators preserve almost all of the geometric properties of Ehrenfest dynamics, in Sec. \[ \text{III} \] we numerically demonstrate the efficiency and geometric properties of these integrators on a four-dimensional extension of the Shin–Metiu model. In this system, the first and second excited adiabatic states are coupled significantly due to a conical intersection. Section \[ \text{IV} \] concludes the paper.

\section{THEORY}

\subsection{Time-dependent Hartree approximation for the molecular wavefunction}

Quantum evolution of a molecule is governed by the time-dependent Schrödinger equation (TDSE)

\begin{equation}
  i\hbar \frac{d}{dt} \Psi_t = \mathcal{H} \Psi_t,
\end{equation}

where \( \Psi_t \) denotes the molecular state at time \( t \) and \( \mathcal{H} \) is the molecular Hamiltonian. In general, we will denote operators acting on both nuclei and electrons by a calligraphic font, whereas the operators acting either only on nuclei or only on electrons will have a hat. The molecular Hamiltonian is equal to the sum

\begin{equation}
  \mathcal{H} = \hat{T}_{nu} + \hat{T}_{el} + V
\end{equation}
of the nuclear kinetic energy operator

\[ \hat{T}_{nu} = \frac{1}{2} \hat{P}^T \cdot M^{-1} \cdot \hat{P}, \tag{3} \]

electronic kinetic energy operator

\[ \hat{T}_{el} = \frac{1}{2} \hat{p}^T \cdot m^{-1} \cdot \hat{p}, \tag{4} \]

and potential energy operator \( V(\hat{q}, \hat{Q}) \). We assume that the nuclear position \( Q \) and momentum \( P \) are \( D \)-dimensional vectors, whereas the electronic position \( q \) and momentum \( p \) are \( d \)-dimensional vectors. The nuclear and electronic mass matrices, \( M \) and \( m \), can, in general, be real symmetric \( D \times D \) and \( d \times d \) matrices, respectively.

The time-dependent Hartree (TDH)\cite{57,58,59,60} approximation is an optimal approximate solution to the molecular TDSE \( \{1\} \) among those in which the molecular state can be written as the Hartree product

\[ \Psi_t = a_t \chi_t \psi_t \tag{5} \]

of the nuclear wavepacket \( \chi_t \) and electronic wavepacket \( \psi_t \); the complex number \( a_t \) is inserted for convenience. In the TDH approximation, obtained by applying the Dirac-Frenkel time-dependent variational principle\cite{57,58,59,60} to ansatz \( \{5\} \), the prefactor evolves as\cite{57}

\[ a_t = e^{iE_t/\hbar}, \tag{6} \]

and the nuclear and electronic states satisfy the system

\[ i\hbar \dot{\chi}_t = \hat{H}_{nu} \chi_t, \tag{7} \]
\[ i\hbar \dot{\psi}_t = \hat{H}_{el} \psi_t \tag{8} \]

of coupled nonlinear Schrödinger equations with mean-field nuclear and electronic Hamiltonian operators

\[ \hat{H}_{nu} := \langle \mathcal{H} \rangle_{\psi_t} = \langle \psi_t | \mathcal{H} | \psi_t \rangle, \tag{9} \]
\[ \hat{H}_{el} := \langle \mathcal{H} \rangle_{\chi_t} = \langle \chi_t | \mathcal{H} | \chi_t \rangle. \tag{10} \]

The mean-field operators satisfy the obvious identity \( \langle \hat{H}_{nu} \rangle_{\chi_t} = \langle \hat{H}_{el} \rangle_{\psi_t} = E \). Note that the solution expressed by Eqs. \( \{6\}-\{8\} \) is unique except for an obvious gauge freedom in redistributing the phase among \( a_t, \chi_t, \) and \( \psi_t \).
B. Mixed quantum-classical limit: Ehrenfest dynamics

In the classical limit for nuclei, the nuclear position and momentum operators \( \hat{Q} \) and \( \hat{P} \) are replaced with classical variables \( Q \) and \( P \). Then, the mean-field nuclear Hamiltonian (9) is no longer an operator, but a phase space function

\[
H_{\text{nu}}(Q, P) = \langle H(Q, P) \rangle_{\psi_t},
\]

where \( H(Q, P) = \hat{T}_{\text{el}} + T_{\text{nu}}(P) + \hat{V}(Q) \), and the mean-field electronic Hamiltonian (10) becomes the molecular Hamiltonian evaluated at the current nuclear positions and momenta:

\[
\hat{H}_{\text{el}}(Q_t, P_t) = H(Q_t, P_t).
\]

We thus obtain the mixed quantum-classical Ehrenfest dynamics, in which the nuclear positions and momenta evolve according to classical Hamilton’s equations of motion with Hamiltonian \( H_{\text{nu}}(Q, P) \), and the electronic state evolves according to the TDSE with a time-dependent Hamiltonian \( \hat{H}_{\text{el}}(Q_t, P_t) \):

\[
\dot{Q}_t = \frac{\partial H_{\text{nu}}(Q_t, P_t)}{\partial P},
\]

\[
\dot{P}_t = -\frac{\partial H_{\text{nu}}(Q_t, P_t)}{\partial Q},
\]

\[
i\hbar \dot{\psi}_t = \hat{H}_{\text{el}}(Q_t, P_t)\psi_t.
\]

Note that these three differential equations are coupled and, moreover, that the electronic TDSE is nonlinear due to this coupling.

Equations (13)–(15) can be re-expressed as more compact Hamilton’s equations

\[
\dot{q}_{\text{eff}, t} = \frac{\partial H_{\text{eff}}(q_{\text{eff}, t}, p_{\text{eff}, t})}{\partial p_{\text{eff}, t}},
\]

\[
\dot{p}_{\text{eff}, t} = -\frac{\partial H_{\text{eff}}(q_{\text{eff}, t}, p_{\text{eff}, t})}{\partial q_{\text{eff}, t}}
\]

associated with an effective mixed quantum-classical Hamiltonian

\[
H_{\text{eff}}(x_{\text{eff}}) := \langle \hat{H}_{\text{el}}(Q, P) \rangle_{\psi}
\]

\[
= \frac{1}{2\hbar} [\langle \hat{H}_{\text{el}}(Q, P) \rangle_{q_\psi} + \langle \hat{H}_{\text{el}}(Q, P) \rangle_{p_\psi}],
\]

acting on an extended, effective mixed quantum-classical phase space with coordinates \( x_{\text{eff}} = (q_{\text{eff}}, p_{\text{eff}}) = (Q, q_\psi, P, p_\psi) \). The “quantum” Darboux coordinates \( (q_\psi, p_\psi) \) consist of the
real and imaginary part of the electronic wavefunction in position representation: \( q_\psi := \sqrt{2\hbar} \text{Re}\psi(q) \) and \( p_\psi := \sqrt{2\hbar} \text{Im}\psi(q) \) (we omit the dependence of \( q_\psi \) and \( p_\psi \) on \( q \) for brevity).

In general, \( q_\psi \) and \( p_\psi \) are real functions in an infinite-dimensional space; therefore, the “quantum” part

\[
\dot{q}_\psi(t) = \frac{\delta H_{\text{eff}}}{\delta p_\psi}(q_{\text{eff}},t,p_{\text{eff}},t), \tag{19}
\]

\[
\dot{p}_\psi(t) = -\frac{\delta H_{\text{eff}}}{\delta q_\psi}(q_{\text{eff}},t,p_{\text{eff}},t) \tag{20}
\]

of Eqs. (16) and (17), in fact, involves partial functional derivatives

\[
\frac{\delta H_{\text{eff}}}{\delta q_\psi} = \frac{1}{2\hbar} \frac{\delta}{\delta q_\psi} \int [q_\psi \hat{H}_{\text{el}}(Q,P)q_\psi + p_\psi \hat{H}_{\text{el}}(Q,P)p_\psi] dq = \hbar^{-1} \hat{H}_{\text{el}}(Q,P)q_\psi, \tag{21}
\]

\[
\frac{\delta H_{\text{eff}}}{\delta p_\psi} = \frac{1}{2\hbar} \frac{\delta}{\delta p_\psi} \int [q_\psi \hat{H}_{\text{el}}(Q,P)q_\psi + p_\psi \hat{H}_{\text{el}}(Q,P)p_\psi] dq = \hbar^{-1} \hat{H}_{\text{el}}(Q,P)p_\psi. \tag{22}
\]

Substituting Eqs. (21) and (22) into Hamilton’s equations (19) and (20) recovers the TDSE (15) for the electronic wavefunction.

In practical calculations, \( q_\psi \) and \( p_\psi \) are usually represented in a finite basis or on a grid as \( N \)-dimensional vectors, where \( N \) is either the size of the basis or number of grid points. In such cases, functional derivatives (21) and (22) reduce to partial derivatives

\[
\frac{\partial H_{\text{eff}}}{\partial q_\psi} = \frac{1}{2\hbar} \frac{\partial}{\partial q_\psi} [q_\psi^T \hat{H}_{\text{el}}(Q,P)q_\psi + p_\psi^T \hat{H}_{\text{el}}(Q,P)p_\psi] = \hbar^{-1} H_{\text{el}}(Q,P)q_\psi, \tag{23}
\]

\[
\frac{\partial H_{\text{eff}}}{\partial p_\psi} = \frac{1}{2\hbar} \frac{\partial}{\partial p_\psi} [q_\psi^T \hat{H}_{\text{el}}(Q,P)q_\psi + p_\psi^T \hat{H}_{\text{el}}(Q,P)p_\psi] = \hbar^{-1} H_{\text{el}}(Q,P)p_\psi, \tag{24}
\]

where \( H_{\text{el}}(Q,P) \) is an \( N \times N \) matrix representation of operator \( \hat{H}_{\text{el}}(Q,P) \).

C. Geometric properties

1. Norm conservation

Ehrenfest dynamics conserves the norm

\[
||\psi_t|| := \langle \psi_t | \psi_t \rangle^{1/2} \tag{25}
\]
of the electronic wavefunction because
\[
\frac{d}{dt} \| \psi_t \|^2 = \langle \dot{\psi}_t | \psi_t \rangle + \langle \psi_t | \dot{\psi}_t \rangle = \frac{i}{\hbar} \left[ \langle \hat{H}_{el}(Q_t, P_t) | \psi_t \rangle - \langle \hat{H}_{el}(Q_t, P_t) \rangle_{\psi_t} \right] = 0,
\]
where we used Eq. (15) and the hermiticity of \( \hat{H}_{el}(Q_t, P_t) \).

2. Energy conservation

The total energy \( E = H_{nu}(Q_t, P_t) = \langle \hat{H}_{el}(Q_t, P_t) | \psi_t \rangle \) of the system is conserved, in general, by the time-dependent variational principle and, in particular, by the TDH approximation. However, because we have also taken the mixed quantum-classical limit, let us verify the conservation of energy explicitly:
\[
\frac{dE}{dt} = \langle \dot{\psi}_t | \dot{\psi}_t \rangle + \langle \dot{\psi}_t | \hat{H}_{el}(Q_t, P_t) | \dot{\psi}_t \rangle + \dot{Q}^T_t \cdot \frac{\partial H_{nu}}{\partial Q}(Q_t, P_t) + \dot{P}^T_t \cdot \frac{\partial H_{nu}}{\partial P}(Q_t, P_t) = \frac{i}{\hbar} \left[ \langle \dot{\psi}_t | \dot{\psi}_t \rangle - \langle \dot{\psi}_t | \dot{\psi}_t \rangle \right] - \dot{Q}^T_t \cdot \dot{Q}_t + \dot{P}^T_t \cdot \dot{P}_t = 0,
\]
where we used the hermiticity of \( \hat{H}_{el}(Q_t, P_t) \) and Eqs. (13)–(15). The energy conservation also follows directly from the effective Hamiltonian structure:
\[
\frac{dE}{dt} = \frac{d}{dt} H_{\text{eff}}(q_{\text{eff}, t}, p_{\text{eff}, t}) = \dot{q}^T_{\text{eff}, t} \frac{\partial H_{\text{eff}}}{\partial q_{\text{eff}, t}}(q_{\text{eff}, t}, p_{\text{eff}, t}) + \dot{p}^T_{\text{eff}, t} \frac{\partial H_{\text{eff}}}{\partial p_{\text{eff}, t}}(q_{\text{eff}, t}, p_{\text{eff}, t}) = -\dot{q}^T_{\text{eff}, t} \dot{p}_{\text{eff}, t} + \dot{p}^T_{\text{eff}, t} \dot{q}_{\text{eff}, t} = 0,
\]
where we used Eqs. (16) and (17).

3. Symplecticity

The effective, mixed quantum-classical symplectic two-form
\[
\omega_{\text{eff}} := dq_{\text{eff}} \wedge dp_{\text{eff}} = \omega_{\text{cl}} + \omega_{\text{qm}}
\]
is a sum of the classical (cl) canonical two-form \( \omega_{\text{cl}} := dQ \wedge dP \) and the quantum (qm) canonical two-form \( \omega_{\text{qm}} := dq_\psi \wedge dp_\psi \), which acts on states \( \psi_1 \) and \( \psi_2 \) as \( \omega_{\text{qm}}(\psi_1, \psi_2) = \)
\[ 2\hbar \text{Im} \langle \psi_1 | \psi_2 \rangle \] (see Appendix B and Refs. 57, 87, and 88). Let \( \Phi_{H,t} : x_{\text{eff},0} \mapsto x_{\text{eff},t} \) denote the Hamiltonian flow of \( H_{\text{eff}} \). The stability (or Jacobian) matrix \( M_t \) of the Hamiltonian flow \( \Phi_{H,t} \) is a symplectic matrix. While this holds in general \( 56,89 \), we show it explicitly for our case in Appendix C. As a result, Ehrenfest dynamics conserves the symplectic two-form \( \omega_{\text{eff}} \) from Eq. (29) (see Appendix C).

4. Time reversibility

An involution is a mapping \( S \) that is its own inverse, i.e., \( S(S(x)) = x \). We will consider the involution

\[
S = \begin{pmatrix}
I_D & 0 \\
0 & -I_D
\end{pmatrix}
\] (30)

that changes the sign of the nuclear momenta and conjugates the electronic wavefunction in position representation (i.e., changes the sign of \( p_\psi \)). Following Ref. 56, we call a flow \( \Phi_t \) time-reversible under a general involution \( S \) if it satisfies

\[
S \Phi_t [ S \Phi_t (x_{\text{eff}}) ] = x_{\text{eff}}.
\] (31)

Because effective Hamiltonian \( H_{\text{eff}} \) is an even function in \( p_{\text{eff}} \), i.e., \( H_{\text{eff}}(x_{\text{eff}}) = H_{\text{eff}}(Sx_{\text{eff}}) \), its Hamiltonian flow satisfies \( 56 \)

\[
\Phi_{H_{\text{eff}},t}(x_{\text{eff}}) = S \Phi_{H_{\text{eff}},-t}(Sx_{\text{eff}}).
\] (32)

Since \( S^{-1} = S \) and, by definition, any flow is symmetric (i.e., \( \Phi_{-t} = \Phi_t^{-1} \)) \( 56,59 \), the satisfaction of Eq. (32) implies the satisfaction of the time reversibility condition (31).

D. Geometric Integrators

As in the split-operator algorithm \( 61,90-92 \) for the TDSE or in the Verlet algorithm \( 62 \) for Hamilton’s equations of motion, we can obtain a symmetric potential-kinetic-potential (VTV) algorithm of the second order in the time step \( \Delta t \) by using the Strang splitting \( 59 \) and performing, in sequence, potential propagation for time \( \Delta t/2 \), kinetic propagation for \( \Delta t \), and potential propagation for \( \Delta t/2 \). The second-order kinetic-potential-kinetic (TVT) algorithm is obtained similarly, by exchanging the potential and kinetic propagations. Either of the two second-order algorithms can be symmetrically composed \( 55,93 \) to obtain an algorithm
of an arbitrary even order of accuracy in $\Delta t$. This is achieved by using the recursive triple-
jump\cite{70,71} or Suzuki-fractal\cite{71} composition schemes, or with a more efficient scheme specific
to each order (which we shall call “optimal”).\cite{71,73,74} We, therefore, only need to present the
analytical solutions of the kinetic and potential propagation steps for arbitrary times $t$.

During the kinetic propagation, the Hamiltonian reduces to

$$\hat{H}(Q, P) = \hat{T}_{\text{el}} + T_{\text{nu}}(P),$$

(33)

and the equations of motion $\eqref{13}-\eqref{15}$ become

$$\dot{Q}_t = M^{-1} \cdot P_t, \quad (34)$$

$$\dot{P}_t = 0, \quad (35)$$

$$i\hbar \dot{\psi}_t = [\hat{T}_{\text{el}} + T_{\text{nu}}(P_t)]\psi_t, \quad (36)$$

which are equivalent to Hamilton’s equations $\eqref{16}$ and $\eqref{17}$ with $H_{\text{eff}} = \langle \hat{T}_{\text{el}} + T_{\text{nu}}(P) \rangle \psi$. Because nuclear momenta $P_t$ do not evolve during the kinetic propagation, Eqs. $\eqref{34}-\eqref{36}$ can be solved analytically to obtain

$$Q_t = Q_0 + tM^{-1} \cdot P_0, \quad (37)$$

$$P_t = P_0, \quad (38)$$

$$\psi_t = e^{-it[\hat{T}_{\text{el}} + T_{\text{nu}}(P_0)]/\hbar}\psi_0. \quad (39)$$

As $\hat{T}_{\text{el}} = T(\hat{p})$, Eq. $\eqref{39}$ is easily evaluated in momentum representation.

During the potential propagation, the Hamiltonian reduces to

$$\hat{H}(Q, P) = \hat{V}(Q),$$

(40)

and the equations of motion $\eqref{13}-\eqref{15}$ become

$$\dot{Q}_t = 0, \quad (41)$$

$$\dot{P}_t = -\langle \hat{V}'(Q_t) \rangle_{\psi_t}, \quad (42)$$

$$i\hbar \dot{\psi}_t = \hat{V}(Q_t)\psi_t, \quad (43)$$

which are equivalent to Hamilton’s equations $\eqref{16}$ and $\eqref{17}$ with $H_{\text{eff}} = \langle \hat{V}(Q) \rangle \psi$. Because nuclear positions $Q_t$ do not evolve during the potential propagation, one can replace $Q_t$ with $Q_0$ in Eqs. $\eqref{42}$ and $\eqref{43}$. Even after the substitution of $Q_t = Q_0$, Eq. $\eqref{42}$ seems hard to
solve due to an apparent coupling to Eq. (43). However, this coupling can be removed by noting that

\[
\langle \hat{V}'(Q_0) \rangle_{\psi_t} = \langle \psi_0 | e^{it\hat{V}(Q_0)/\hbar} \hat{V}'(Q_0) e^{-it\hat{V}(Q_0)/\hbar} | \psi_0 \rangle
= \langle \psi_0 | e^{it\hat{V}(Q_0)/\hbar} e^{-it\hat{V}(Q_0)/\hbar} \hat{V}'(Q_0) | \psi_0 \rangle
= \langle \hat{V}'(Q_0) \rangle_{\psi_0}.
\] (44)

As a result, Eqs. (41)–(43) can be solved analytically to obtain

\[
Q_t = Q_0, \quad (45)
\]
\[
P_t = P_0 - t \langle \hat{V}'(Q_0) \rangle_{\psi_0}, \quad (46)
\]
\[
\psi_t = e^{-it\hat{V}(Q_0)/\hbar} \psi_0. \quad (47)
\]

As \( \hat{V}(Q) = V(\hat{q}, Q) \), Eq. (47) is easily evaluated in position representation.

E. Geometric properties of the geometric integrator

Like all other integrators obtained with the splitting method, in the proposed algorithm, each potential or kinetic step of the Ehrenfest dynamics is solved exactly, and each of these steps has all the geometric properties of the exact solution. The second-order Strang splitting method, composed from two exact flows, or any of its symmetric compositions preserves all the listed geometric properties except the conservation of energy (see, e.g., Refs. 55 and 56 or Refs. 91–93 and references therein).

III. NUMERICAL EXAMPLE

We use a low-dimensional model that is solvable “numerically” exactly to demonstrate the geometric and convergence properties of the presented integrators. Since the high efficiency and geometric properties of these integrators are most meaningful when the mean-field Ehrenfest approximation is valid, we have chosen the system and initial state carefully so that numerically converged Ehrenfest and exact quantum simulations yield similar results. At the same time, we have ensured that the resulting nonadiabatic simulation describes a realistic light-induced excitation. (See references in Sec. I for higher-dimensional examples where the Ehrenfest approximation was employed successfully.)
The four-dimensional extension of the Shin–Metiu model consists of an interacting electron and proton, both moving in two spatial dimensions and feeling an additional field of two fixed protons (all three protons are distinguishable). The four-dimensional ($D = 2$, $d = 2$) model Hamiltonian is of form (2) with

$$V = V_{\text{quartic}}(\hat{Q}) + V^{\text{en}}(|\hat{q} - Q_a|) + V^{\text{en}}(|\hat{q} - Q_b|)$$

$$+ V^{\text{en}}(|\hat{q} - \hat{Q}|) + V^{\text{en}}(|\hat{Q} - Q_a|)$$

$$+ V^{\text{en}}(|\hat{Q} - Q_b|) + V^{\text{en}}(|Q_a - Q_b|),$$

where $Q_a = (-L/2, 0)$ and $Q_b = (L/2, 0)$ are the positions of the two fixed protons, and

$$V^{\text{en}}(\xi) = -1/\sqrt{a + \xi^2}$$

$$V^{\text{nn}}(\xi) = 1/\sqrt{b + \xi^2}$$

are attractive and repulsive regularized Coulomb potentials; following Ref. [75], we take $L = 4\sqrt{3}/5$ a.u., $a = 0.5$ (a.u.)$^2$, and $b = 10$ (a.u.)$^2$. Quartic potential $V_{\text{quartic}}(Q) = (|Q|/Q_c)^4$ with $Q_c = 3.5$ a.u. ensures that the system remains bound.

For the dynamics, we considered the initial state

$$\Psi_0(q, Q) = \chi_{\text{gwp}}(Q - Q_0)\varphi_2(q; Q),$$

where $\varphi_i$ is the $i$th excited adiabatic electronic state, and

$$\chi_{\text{gwp}}(Q) = \frac{1}{\sqrt{\pi \hbar \sigma^2}} e^{-Q^2/(2\hbar \sigma^2)}$$

is the ground vibrational eigenstate of a harmonic fit to the ground electronic state; here, $\sigma = 0.24$ a.u. The displacement of the initial wavepacket by $Q_0 = (0.5 \text{ a.u.}, 1.5 \text{ a.u.})$ from the ground state equilibrium is motivated by the displaced excitation of molecules: Suppose state $\varphi_2$ is dark; then a wavepacket may reach it at a nuclear geometry that is not the ground state equilibrium via an intersection with a bright state. To obtain $\varphi_2(q; Q)$, we solved the electronic time-independent Schrödinger equation

$$[\hat{T}_{\text{el}} + \hat{V}(Q)]\varphi_i(Q) = E_i(Q)\varphi_i(Q),$$

where $\hat{T}_{\text{el}} = T(\hat{p})$ and $\hat{V}(Q) = V(\hat{q}, Q)$ are operators acting on electrons; in position representation, Eq. (53) takes a more familiar form

$$\left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial q^2} + V(q; Q)\right] \varphi_i(q; Q) = E_i(Q)\varphi_i(q; Q).$$
FIG. 1. Potential energy surfaces in the vicinity of the conical intersection at $Q = Q_{CI} = (0, 1.2 \text{ a.u.})$ in the model system from Sec. III. Energies $E_i(Q) := \langle \varphi_i(Q) | \hat{T}_{el} + \hat{V}(Q) | \varphi_i(Q) \rangle$ of the first ($i = 1$) and second ($i = 2$) excited adiabatic electronic states $\varphi_i(Q)$ are shown in green and red, respectively. Section S1 of the supplementary material describes the method we employed to solve this equation.

Because our approach does not rely on a specific electronic basis (such as the basis of adiabatic or diabatic electronic states) to represent the molecular wavepacket, the initial state can be a general function of $q$ and $Q$. To be specific, however, we chose to start the dynamics from a single excited adiabatic electronic state (here $\varphi_2$), which is the most common choice in the literature studying nonadiabatic dynamics following a light-induced excitation. In the model described by Eqs. (48)–(50), the second excited adiabatic state $\varphi_2$ is, indeed, significantly coupled to the first excited state $\varphi_1$ by a conical intersection depicted in Fig. 1.

In Fig. 2 we compare the exact quantum dynamics $\Psi_t = \exp(-it\hat{H}/\hbar)\Psi_0$ with Ehrenfest dynamics $x_{eff,t} = \Phi_{H_{eff,t}}(x_{eff,0})$. The initial state of the system is $(Q_t, P_t, \psi_t)|_{t=0} = (Q_0, 0, \varphi_2(Q_0))$ and the corresponding initial mixed quantum-classical phase space point

$$x_{eff,0} = (Q_0, \sqrt{2}\hbar \text{Re}\varphi_2(q; Q_0), 0, 0) \quad (55)$$

can be thought of as state (51) with an infinitesimally narrow Gaussian wavepacket; the fourth component in Eq. (55) is zero because the state $\varphi_2(q; Q_0)$, in position representation, is purely real: $\text{Im}\varphi_2(q; Q_0) = 0$. We compare three observables: nuclear position $Q(t)$, adiabatic population $P_i(t)$, and electronic density $\rho_{el}(q, t)$. In quantum dynamics, they are
obtained from the full wavefunction $\Psi_t$ as:

$$ Q(t) = \langle \hat{Q} \rangle_{\Psi_t}, \quad (56) $$

$$ P_i(t) = \langle \hat{P}_i \rangle_{\Psi_t}, \quad (57) $$

$$ \rho_{\text{el}}(q,t) = \int dQ |\Psi_t(q,Q)|^2. \quad (58) $$

To find population $P_i(t)$ from Eq. (57), we computed the expectation value of the population operator $\hat{P}_i := |\varphi_i\rangle \langle \varphi_i|$ in position representation:

$$ \langle \hat{P}_i \rangle_{\Psi_t} = \int \left| \int \varphi_i(q;Q)^* \Psi_t(q,Q) dq \right|^2 dQ. \quad (59) $$

In Ehrenfest dynamics, the nuclear position $Q(t)$ is simply the current position $Q_t$ of the trajectory, whereas the adiabatic population $P_i(t) = |\langle \varphi_i(Q_t) | \psi_t \rangle|^2$ and electronic density $\rho_{\text{el}}(q,t) = |\psi_t(q)|^2$ depend on the electronic wavefunction $\psi_t$.

Figure 2 shows that during the considered time interval $t \in [0,t_f]$ with $t_f = 170$ a.u., Ehrenfest dynamics yields qualitatively correct results. In particular, the nuclear motion towards the conical intersection at $Q = Q_{\text{CI}} = (0,1.2 \text{ a.u.})$ [panels (a) and (b)] and the resulting population transfer from the initial second excited to the first excited state [panels (c) and (d)] are well described by Ehrenfest dynamics. The electronic densities obtained from the exact quantum and Ehrenfest dynamics [panels (e) and (f)] at the final time $t = t_f$ are also very similar. The mean-field Ehrenfest approximation works well because the nuclear density remains localized (not shown) and the electronic density is almost stationary.

In the following, we demonstrate the geometric properties and high efficiency of high-order geometric integrators (from Sec. II D). Owing to the low electronic dimensionality ($d = 2$) of the employed model, we could ensure that the numerical errors due to the representation of the electronic wavefunction $\psi_t(q)$ were negligible in comparison with the time propagation errors: The wavefunction was represented, with high accuracy, on a uniform grid (see Sec. S1 of the supplementary material for computational details). This approach, however, would be too computationally demanding in practical, higher-dimensional (i.e., larger $d$) simulations. Instead, for such simulations, one of the real-time time-dependent electronic structure methods, such as real-time time-dependent Hartree–Fock (TDHF) and real-time time-dependent density functional theory (TDDFT) should be employed. In particular, because there are existing implementations of real-time TDDFT using the split-operator algorithms for the propagation of Kohn–Sham orbitals, it should be straightforward to
FIG. 2. Comparison of Ehrenfest dynamics with the exact quantum dynamics. (a)–(d): Time dependence of nuclear position $Q_n(t)$ [$n = 1$ in panel (a), $n = 2$ in panel (b)] and of the first and second excited adiabatic populations $P_i(t)$ [$i = 1$ in panel (c), $i = 2$ in panel (d)]. (e) and (f): Electronic densities at the final time $t = t_f$ obtained from quantum dynamics [panel (e)] and Ehrenfest dynamics [panel (f)].

employ the presented integrators for TDDFT-Ehrenfest simulations. However, the exact efficiency of the high-order geometric integrators when applied to realistic TDDFT-Ehrenfest simulations is hard to predict and is outside the scope of this study.

In Fig. 3 we demonstrate the geometric properties of the presented integrators (in all figures, we omit the results of the TVT algorithm and its compositions because they are nearly identical to the corresponding results for the VTV algorithm). The figure shows that the norm of the electronic wavefunction [panels (a) and (b)], time reversibility [panels (c) and (d)], and symplecticity [panels (e) and (f)] are conserved as functions of time [for a fixed time step $\Delta t = 0.5$ a.u., panels (a), (c), and (e)] and regardless of the time step $\Delta t$ used [for a fixed final time $t_f = 170$ a.u., panels (b), (d), and (f)]. We check the symplecticity of stability matrix $M_t$ by measuring the Frobenius distance

$$d_t = \| M_t^T J M_t - J \|$$

of $M_t^T J M_t$ from $J$ (see Appendix C). Here,

$$J := \begin{pmatrix} 0 & -I_{D+N} \\ I_{D+N} & 0 \end{pmatrix}$$

(61)
is the standard symplectic matrix, and the Frobenius norm is defined as \( \|A\| := \langle A, A \rangle^{1/2} \),
where \( \langle A, B \rangle := \text{Tr}(A^\dagger B) \). Time reversibility of an approximate method that approximates
the exact flow \( \Phi_t \) at discrete times \( t = n\Delta t \) (\( n \) integer) by an iterated map \( \Phi^{(\Delta t)}_{\text{appr},t} := (\Phi^{(\Delta t)}_{\text{appr}})^n : x_{\text{eff},0} \mapsto x^{(\Delta t)}_{\text{eff},t} \) is measured by the distance
\[
T_t := \|x^{\text{fb},t}_{\text{eff}} - x_{\text{eff},0}\| \tag{62}
\]
of the forward-backward propagated state \( x^{\text{fb},t}_{\text{eff}} := S\Phi^{(\Delta t)}_{\text{appr},t}S\Phi^{(\Delta t)}_{\text{appr},t}(x_{\text{eff},0}) \) from the initial state \( x_{\text{eff},0} \). The norm \( \|x_{\text{eff}}\| := \langle x_{\text{eff}}, x_{\text{eff}} \rangle^{1/2} \) of an effective phase space point \( x_{\text{eff}} \) is defined
using the scalar product \( \langle x_{\text{eff},1}, x_{\text{eff},2} \rangle := Q^T_1 \cdot Q_2 + P^T_1 \cdot P_2 + \langle \psi_1 | \psi_2 \rangle \) of \( x_{\text{eff},1} \) and \( x_{\text{eff},2} \). The corresponding squared “distance” \( \|x_{\text{eff},1} - x_{\text{eff},2}\|^2 \) between points \( x_{\text{eff},1} \) and \( x_{\text{eff},2} \) is simply
the sum \( \|Q_1 - Q_2\|^2 + \|P_1 - P_2\|^2 + \|\psi_1 - \psi_2\|^2 \) of the squared distances between \( Q_1 \) and \( Q_2 \), between \( P_1 \) and \( P_2 \), and between \( \psi_1 \) and \( \psi_2 \).

Panels (g) and (h) of Fig. 3 show that the energy is only conserved approximately, to
the same order as the order of convergence of the integrator. The loss of exact energy
conservation is standard for any splitting method and is due to alternating kinetic and
potential propagations: the effective Hamiltonian alternates between \( H_{\text{eff}} = \langle \hat{T}_{\text{el}} + T_{\text{nu}}(P) \rangle_{\psi} \)
and \( H_{\text{eff}} = \langle \hat{V}(Q) \rangle_{\psi} \), and its time-dependent nature breaks the conservation of energy.

Figure 4 confirms the predicted asymptotic order of convergence of the geometric inte-
grators. However, panel (c) may wrongly suggest that the Suzuki-fractal scheme leads to
the most efficient method, as it has the smallest error for each time step size. What Fig. 4
does not show is that the sixth-order Suzuki-fractal scheme has a factor of \( 25/9 \) more sub-
steps per time step than either the triple-jump or optimal scheme. If we instead consider
the dependence of the convergence error on the computational cost [measured by the cen-
tral processing unit (CPU) time], the optimal composition scheme indeed yields the most
efficient method for each order of accuracy (see Fig. S1 in Sec. S2 of the supplementary
material).

To reach a modest convergence error of \( 10^{-3} \), the most efficient geometric integrator
(obtained using the optimal fourth-order composition scheme) is 15 times faster than the
two time step method and roughly twice slower than the three time step method (see Fig. 5).
Yet, a clear advantage of the geometric integrators over the other methods is the exact
conservation of geometric properties. Both the two and three time step methods violate
symplecticity; the two time step method, in addition, violates time reversibility (see Fig. 6
FIG. 3. Conservation of geometric properties by the geometric integrators presented in Sec. II D. (a) and (b): Norm of the electronic wavefunction. (c) and (d): Time reversibility [Eq. (62)]. (e) and (f): Symplecticity [Eq. (60)]. (g) and (h): Energy. Both the time dependence of the geometric properties for a fixed time step $\Delta t = 0.5$ a.u. [left-hand side panels (a), (c), (e), and (g)] and the geometric properties at the final time, $t = t_f = 170$ a.u., as functions of $\Delta t$ [right-hand side panels (b), (d), (f), and (h)] are shown. The costly numerical propagation of stability matrix $M_t$ is done separately from the main Ehrenfest dynamics (see Appendix D). Due to prohibitive computational cost, only the elementary second-order method is presented in panels (e) and (f); however, all of its compositions are symplectic regardless of the time step (as justified in Sec. II E). Initial energy of the system is $E_0 = -0.2$ a.u. To avoid clutter, only the higher-order integrators obtained using the optimal composition schemes are shown (the Suzuki-fractal scheme is the optimal fourth-order scheme).
FIG. 4. Convergence of geometric integrators for Ehrenfest dynamics measured by the convergence error of the final effective phase space point \( x_{\text{eff},t_f} \) as a function of \( \Delta t \). Gray straight lines indicate various predicted orders of convergence \( O(\Delta t^n) \). (a) Methods obtained using the optimal composition schemes, i.e., methods presented in Fig. 3. (b) Zoomed-in version of panel (a), highlighting the asymptotic orders of convergence of the integrators. (c) Sixth-order methods obtained using the triple jump, Suzuki-fractal, and optimal composition schemes. The error of an approximate method is measured by the distance \( \| x_{\text{eff},t_f}^{(\Delta t)} - x_{\text{eff},t_f}^{(\Delta t/2)} \| \) of the final point \( x_{\text{eff},t_f}^{(\Delta t)} = \Phi_{\text{appr},t_f}^{(\Delta t)}(x_{\text{eff},0}) \), obtained with time step \( \Delta t \), from the final point \( x_{\text{eff},t_f}^{(\Delta t/2)} = \Phi_{\text{appr},t_f}^{(\Delta t/2)}(x_{\text{eff},0}) \), obtained with half time step \( \Delta t/2 \).

IV. CONCLUSION

We have demonstrated that the high-order geometric integrators for Ehrenfest dynamics can be obtained by simultaneously employing the splitting and composition methods. Since Ehrenfest dynamics already involves a rather severe approximation, one is often not interested in numerically converged solutions. In such cases, geometric integrators become much more relevant because only they guarantee the exact conservation of the geometric invariants regardless of the accuracy of the solution.
FIG. 5. Efficiency of the geometric integrators is compared with the efficiency of the widely-used two time step and three time step methods. Efficiency is measured using the dependence of the convergence error on the computational cost. Only the higher-order geometric integrators obtained using the optimal composition schemes are shown, for they are the most efficient for each order of accuracy.

That is not to say that the high-order geometric integrators are inefficient for high accuracy simulations. On the contrary, to reach an error of, e.g., $10^{-6}$, using the eighth-order geometric integrator yields a four-fold speedup over the three time step method (see Fig. 5) and a 5000-fold speedup over the two time step method. High-accuracy results with negligible numerical errors may be desirable when the error introduced by the mean-field Ehrenfest approximation is either very small or unknown.

SUPPLEMENTARY MATERIAL

See the supplementary material for the computational details (Sec. S1), efficiency of the high-order geometric integrators obtained using the triple-jump, Suzuki-fractal, optimal composition schemes (Sec. S2), and detailed algorithms of the two and three time step methods (Sec. S3).

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AUTHOR DECLARATIONS

Conflict of interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are openly available in Zenodo at https://doi.org/10.5281/zenodo.5167211.

Appendix A: Two and three time step methods

1. Two time step method

Unlike the geometric integrators, which propagate $Q_t, P_t$, and $\psi_t$ simultaneously, the two time step method consists in alternately propagating the classical nuclear phase space point and electronic wavefunction. The time step $\Delta t_{el} = \Delta t/n_{el}$ for the electronic propagation is typically much smaller than the time step $\Delta t$ for the nuclear propagation (we used $n_{el} = 100$).

In the two time step method, we employed the second-order Verlet algorithm to propagate the nuclear phase space point and the second-order VTV split-operator algorithm to propagate the electronic wavefunction. However, because the nuclear phase space point and electronic wavefunction are propagated separately and alternately, the overall two time step method is only first-order accurate in the time step. Moreover, the method is neither time-reversible nor symplectic (see Fig. 6). See Sec. S3 of the supplementary material for the detailed algorithm of the two time step method.
2. Three time step method

The three time step method\cite{13, 54} owing to its symmetry, is both time-reversible and second-order accurate in the time step.\cite{55} However, the method is still not symplectic (see Fig. 6).

In addition to the nuclear time step $\Delta t$ and electronic time step $\Delta t_{el}$, used also in the two time step method, the three time step method improves the efficiency by introducing the intermediate nuclear-electronic coupling time step $\Delta t_{nu-el} = \Delta t/n_{nu-el} = \Delta t_{el}/n_{nu-el}$ (we used $n_{nu-el} = 10$). See Sec. S3 of the supplementary material for the detailed algorithm of the three time step method.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure6}
\caption{Violations of (a) time reversibility [see Eq. (62)] and (b) symplecticity [see Eq. (60)] by the non-geometric integrators: The two time step method is neither reversible nor symplectic, whereas the three time step method is time-reversible but not symplectic. The geometric integrators exactly preserve both (c) time-reversibility and (d) symplecticity. Time step $\Delta t = 17$ a.u. was used. For the two and three time step methods, the corresponding convergence errors are 0.5 and 0.09, respectively, and for all of the presented geometric integrators, the errors are $> 1.4$.}
\end{figure}

Appendix B: Quantum canonical two-form

The canonical two-form $dq_\psi \wedge dp_\psi$ acts on states $\psi_1$ and $\psi_2$ as

$$dq_\psi \wedge dp_\psi(\psi_1, \psi_2) = 2\hbar \text{Im} \psi_1 | \psi_2$$

(B1)
because

\[ dq_\psi \wedge dp_\psi (\psi_1, \psi_2) \]
\[ = \langle dq_\psi (\psi_1) | dp_\psi (\psi_2) \rangle - \langle dp_\psi (\psi_1) | dq_\psi (\psi_2) \rangle \]
\[ = 2\hbar [\langle \text{Re} \psi_1 (q) | \text{Im} \psi_2 (q) \rangle - \langle \text{Im} \psi_1 (q) | \text{Re} \psi_2 (q) \rangle] \]
\[ = 2\hbar \text{Im} \langle \psi_1 | \psi_2 \rangle, \quad (B2) \]

where we have used that the tangent space of a vector space can be identified with the vector space itself,\(^{112}\) i.e.,

\[ dq_\psi (\psi) = q_\psi = \sqrt{2\hbar} \text{Re} \psi (q), \quad (B3) \]
\[ dp_\psi (\psi) = p_\psi = \sqrt{2\hbar} \text{Im} \psi (q). \quad (B4) \]

**Appendix C: Symplecticity of the exact Hamiltonian flow**

We use the standard symplectic matrix

\[ J := \begin{pmatrix} 0 & -I_{D+N} \\ I_{D+N} & 0 \end{pmatrix} \quad (C1) \]

and re-express effective symplectic two-form \(^{29}\) as\(^{56}\)

\[ \omega_{\text{eff}} = \frac{1}{2} (J dx_{\text{eff}}) \wedge dx_{\text{eff}}. \quad (C2) \]

Since \( dx_{\text{eff},t} = M_t dx_{\text{eff},0} \), we have

\[ (J dx_{\text{eff},t}) \wedge dx_{\text{eff},t} = (JM_t dx_{\text{eff},0}) \wedge (M_t dx_{\text{eff},0}) \]
\[ = (M_t^T JM_t dx_{\text{eff},0}) \wedge dx_{\text{eff},0}, \quad (C3) \]

and two-form \( \omega_{\text{eff}} \) is conserved [i.e., \( (J dx_{\text{eff},t}) \wedge dx_{\text{eff},t} = (J dx_{\text{eff},0}) \wedge dx_{\text{eff},0} \)] if \( M_t \) is a symplectic matrix, i.e., if it satisfies the condition

\[ M_t^T J M_t = J. \quad (C4) \]

Since \( M_0 = I \), Eq. \((C4)\) is trivially satisfied at \( t = 0 \). To show that the stability matrix \( M_t \) of Hamiltonian flow \( \Phi_{H_{\text{eff}},t} \) is symplectic, we therefore only have to show that
\[
\frac{d}{dt} M_t^T J M_t = \dot{M}_t^T J M_t + M_t^T \dot{J} M_t
\]
\[
= M_t^T \text{Hess}[H_{\text{eff}}(x_{\text{eff}}, t)] J^2 M_t
\]
\[
+ M_t^T J J^T \text{Hess}[H_{\text{eff}}(x_{\text{eff}}, t)] M_t
\]
\[
= -M_t^T \text{Hess}[H_{\text{eff}}(x_{\text{eff}}, t)] M_t
\]
\[
+ M_t^T \text{Hess}[H_{\text{eff}}(x_{\text{eff}}, t)] M_t
\]
\[
= 0,
\]
(C5)

where we have used the fact that the time derivative of the stability matrix satisfies

\[
\frac{d}{dt} M_t = J^T \text{Hess}[H_{\text{eff}}(x_{\text{eff}}, t)] M_t.
\]
(C6)

Although we did not need the explicit form

\[
\text{Hess}[H_{\text{eff}}(x_{\text{eff}})] =
\begin{pmatrix}
\langle \text{Hess} \dot{V}(Q) \rangle_{\psi} & d_V(Q)q_{\psi} & 0 & d_V(Q)p_{\psi} \\
d_V(Q)q_{\psi} & \dot{H}_{\text{el}}(Q, P) / \hbar & d_T(P)q_{\psi} & 0 \\
0 & d_T(P)q_{\psi} & 1 / M & d_T(P)p_{\psi} \\
d_V(Q)p_{\psi} & 0 & d_T(P)p_{\psi} & \dot{H}_{\text{el}}(Q, P) / \hbar
\end{pmatrix}
\]
(C7)

of the Hessian of \(H_{\text{eff}}(x_{\text{eff}})\) to prove the symplecticity of \(M_t\), this expression will be useful for the numerical propagation of the stability matrix; we defined and used

\[
d_V(Q) := \dot{V}'(Q) / \hbar,
\]
(C8)
\[
d_T(P) := P / (\hbar M)
\]
(C9)

to simplify Eq. [C7].

Appendix D: Numerical propagation of the stability matrix

The numerical propagation of stability matrix \(M_t\) requires much more computational effort than the propagation of mixed quantum-classical phase space point \(x_{\text{eff}}\). It is, in general, not necessary to propagate the stability matrix to simulate Ehrenfest dynamics. Yet, to numerically demonstrate the symplecticity of the geometric integrators, i.e., to prepare
panels (e) and (f) of Fig. 3 we propagated also the stability matrix. Like in the propagation of \( x_{\text{eff}} \), we only need to present the analytical solutions of the kinetic and potential propagation steps for arbitrary times \( t \) because all presented geometric integrators are composed of kinetic and potential propagations (see Sec. III D).

During the kinetic propagation, the equation of motion

\[
\dot{M}_t = J^T \text{Hess}[\langle \hat{T}_{\text{nu+el}}(P_t) \rangle_{\psi}] M_t
\]

for stability matrix \( M_t \) is obtained by reducing the effective Hamiltonian to \( H_{\text{eff}}(x_{\text{eff}}) = \langle \hat{T}_{\text{nu+el}}(P) \rangle_{\psi} = \langle T_{\text{nu}}(P) + \hat{T}_{\text{el}} \rangle \psi \) in Eq. (C6). The explicit form of the Hessian is

\[
\text{Hess}[\langle \hat{T}_{\text{nu+el}}(P) \rangle_{\psi}] = \begin{pmatrix}
0 & 0 & 0 & 0 \\
0 & \hat{T}_{\text{nu+el}}(P)/\hbar & d_T(P)q_\psi & 0 \\
0 & d_T(P)q_\psi & 1/M & d_T(P)p_\psi \\
0 & 0 & d_T(P)p_\psi & \hat{T}_{\text{nu+el}}(P)/\hbar
\end{pmatrix},
\]

and Eq. (D1) can be solved analytically to yield

\[
M_t = \begin{pmatrix}
1 & td_T(P_0)q_{\psi,0} & t/M & td_T(P_0)p_{\psi,0} \\
0 & c_T(P_0) & td_T(P_0)p_{\psi,t} & s_T(P_0) \\
0 & 0 & 1 & 0 \\
0 & -s_T(P_0) & -td_T(P_0)q_{\psi,t} & c_T(P_0)
\end{pmatrix} M_0,
\]

where

\[
c_T(P) := \cos[\hat{T}_{\text{nu+el}}(P)t/\hbar], \quad \text{(D4)}
\]

\[
s_T(P) := \sin[\hat{T}_{\text{nu+el}}(P)t/\hbar], \quad \text{(D5)}
\]

and the propagation of quantum Darboux coordinates

\[
q_{\psi,t} = c_T(P_0)q_{\psi,0} + s_T(P_0)p_{\psi,0}, \quad \text{(D6)}
\]

\[
p_{\psi,t} = -s_T(P_0)q_{\psi,0} + c_T(P_0)p_{\psi,0} \quad \text{(D7)}
\]

for time \( t \) is equivalent to the standard propagation of electronic wavefunction \( \psi_t = \exp[-i\hat{T}_{\text{nu+el}}(P_0)/\hbar]\psi_0 \) since \( \psi_t = (q_{\psi,t} + ip_{\psi,t})/\sqrt{2\hbar} \) since \( \psi_t = (q_{\psi,t} + ip_{\psi,t})/\sqrt{2\hbar} \).
During the potential propagation, the equation of motion
\[ \dot{M}_t = J^T \text{Hess}[\langle \hat{V}(Q_t) \rangle_\psi] M_t \] (D8)
for stability matrix \( M_t \) is obtained by reducing the effective Hamiltonian to \( H_{\text{eff}}(x_{\text{eff}}) = \langle \hat{V}(Q) \rangle_\psi \) in Eq. (C6). The explicit form of the Hessian is
\[
\text{Hess}[\langle \hat{V}(Q) \rangle_\psi] = \\
\begin{pmatrix}
\langle \text{Hess} \hat{V}(Q) \rangle_\psi & d_V(Q)q_\psi & 0 & d_V(Q)p_\psi \\
d_V(Q)q_\psi & \hat{V}(Q)/\hbar & 0 & 0 \\
0 & 0 & 0 & 0 \\
d_V(Q)p_\psi & 0 & 0 & \hat{V}(Q)/\hbar
\end{pmatrix},
\] (D9)
and Eq. (D8) can be solved analytically to yield
\[ M_t = \\
\begin{pmatrix}
1 & 0 & 0 & 0 & 0 \\
0 & c_V(Q_0) & 0 & s_V(Q_0) & 0 \\
td_V(Q_0)p_{\psi,t} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0
\end{pmatrix} \begin{pmatrix}
M_0, \\
0, \\
0, \\
0, \\
0
\end{pmatrix}
\] (D10)
where
\[
c_V(Q) := \cos[\hat{V}(Q)t/\hbar],
\] (D11)
\[
s_V(Q) := \sin[\hat{V}(Q)t/\hbar],
\] (D12)
and the propagation of quantum Darboux coordinates
\[ q_{\psi,t} = c_V(Q_0)q_{\psi,0} + s_V(Q_0)p_{\psi,0}, \] (D13)
\[ p_{\psi,t} = -s_V(Q_0)q_{\psi,0} + c_V(Q_0)p_{\psi,0} \] (D14)
for time \( t \) is equivalent to the propagation of the electronic wavefunction \( \psi_t = \exp[-it\hat{V}(Q_0)/\hbar]\psi_0 \) since \( \psi_t = (q_{\psi,t} + ip_{\psi,t})/\sqrt{2\hbar} \).
**Supplementary material for:**
**High-order geometric integrators for representation-free Ehrenfest dynamics**

This document provides information supporting the main text. It contains the computational details (Sec. S1), efficiency of the high-order geometric integrators obtained using the triple-jump, Suzuki-fractal, and optimal composition schemes (Sec. S2), and detailed algorithms of the two and three time step methods (Sec. S3).

**S1. COMPUTATIONAL DETAILS**

In the exact quantum simulation, the full wavefunction $\Psi_t$ was represented on a uniform four-dimensional grid that is a tensor product of two different two-dimensional grids for the nuclear and electronic degrees of freedom. A uniform grid of 101 × 101 points defined between $Q_n = -3$ a.u. and $Q_n = 3$ a.u. was used for the nuclear degrees of freedom. As for the electronic degrees of freedom, a uniform grid of 64 × 64 points defined between $q_n = -10$ a.u. and $q_n = 10$ a.u. was used; this grid was also used to represent the electronic wavefunction in Ehrenfest simulations. We employed the second-order VTV split-operator algorithm with time step $\Delta t = 0.1$ a.u. for the numerical propagation of $\Psi_t$.

To obtain the initial states, we solved the electronic time-independent Schrödinger equation [Eq. (53) of the main text] with the imaginary time propagation method.\textsuperscript{[113]} To prepare quantum initial state (51) of the main text, we solved the equation at every point on the nuclear grid. In contrast, to obtain the initial effective phase space point for Ehrenfest simulations [see Eq. (55) of the main text], we only had to solve the equation once at the initial nuclear position $Q_0$. 
S2. EFFICIENCY OF THE GEOMETRIC INTEGRATORS

FIG. S1. Efficiency of the geometric integrators presented in Sec. IID of the main text. Like in the main text, efficiency is measured using the dependence of the convergence error on the computational cost (which we measure by CPU time). As expected, for each order of accuracy, the optimal composition scheme yields the most efficient method.

S3. DETAILED ALGORITHMS OF THE TWO AND THREE TIME STEP METHODS

A. Two time step method

The detailed algorithm of the two time step method is as follows (like in the main text, $\Delta t_{\text{el}} = \Delta t/n_{\text{el}}$):

Verlet algorithm with time step $\Delta t$:

\[
\begin{align*}
P_{t+\Delta t/2} &= P_t - \frac{\Delta t}{2} \langle \hat{V}'(Q_t) \rangle \psi_t \\
Q_{t+\Delta t} &= Q_t + \Delta t M^{-1} \cdot P_{t+\Delta t/2} \\
P_{t+\Delta t} &= P_{t+\Delta t/2} - \frac{\Delta t}{2} \langle \hat{V}'(Q_{t+\Delta t}) \rangle \psi_t
\end{align*}
\]

Do $i = 1, \ldots, n_{\text{el}}$

VTV split-operator algorithm with time step $\Delta t_{\text{el}}$:

\[
\psi_{t+\Delta t_{\text{el}}} = \hat{U}_{\text{VTV}}^{(\Delta t_{\text{el}})}(Q_{t+\Delta t}, P_{t+\Delta t}) \psi_{t+(i-1)\Delta t_{\text{el}}}
\]

End Do,
where the evolution operator
\[ \hat{U}_{\text{VT}}^{(\tau)}(Q, P) = \hat{U}_{\nu}^{(\tau/2)}(Q) \hat{U}_{\nu}^{(\tau)}(P) \hat{U}_{\nu}^{(\tau/2)}(Q) \]  
(S1)
for the VTV split-operator algorithm is composed of the potential and kinetic propagation steps,
\[ \hat{U}_{\nu}^{(\tau)}(Q) = \exp \left[ -i\tau \hat{V}(Q) / \hbar \right], \]  
(S2)
\[ \hat{U}_{\nu}^{(\tau)}(P) = \exp \left[ -i\tau \hat{T}_{\text{nu}}(P) / \hbar \right]; \]  
(S3)
here, \( \hat{T}_{\text{nu}}(P) = T_{\text{nu}}(P) + \hat{T}_{\text{el}} \).

B. Three time step method

The detailed algorithm of the three time step method is as follows (like in the main text, \( \Delta t_{\text{nu-el}} = \Delta t / n_{\text{nu-el}} = \Delta t_{\text{el}} n_{\text{el}} / n_{\text{nu-el}} \)):

(Propagation of nuclear momentum by \( \Delta t/2 \))
\[ P_{t+\Delta t/2} = P_t - \frac{\Delta t}{2} \langle \hat{V}'(Q_t) \rangle \psi_t. \]

Do \( i = 1, \ldots, n_{\text{nu-el}} \)

(Propagation of nuclear position by \( \Delta t_{\text{nu-el}}/2 \))
\[ Q_{t+(2i-1)\Delta t_{\text{nu-el}}/2} = Q_{t+(i-1)\Delta t_{\text{nu-el}}} + \frac{\Delta t_{\text{nu-el}}}{2} M^{-1} \cdot P_{t+\Delta t/2} \]

Do \( j = 1, \ldots, n_{\text{el}} / n_{\text{nu-el}} \)

(VTV split-operator algorithm with the time step of \( \Delta t_{\text{el}} \))
\[ \psi_{t+(i-1)\Delta t_{\text{nu-el}}+j\Delta t_{\text{el}}} = \hat{U}_{\text{VT}}^{(\Delta t_{\text{el}})} (Q_{t+(2i-1)\Delta t_{\text{nu-el}}/2}, P_{t+\Delta t/2}) \psi_{t+(i-1)\Delta t_{\text{nu-el}}+(j-1)\Delta t_{\text{el}}}. \]
End Do

(Propagation of nuclear position by \( \Delta t_{\text{nu-el}}/2 \))
\[ Q_{t+i\Delta t_{\text{nu-el}}} = Q_{t+(2i-1)\Delta t_{\text{nu-el}}/2} + \frac{\Delta t_{\text{nu-el}}}{2} M^{-1} \cdot P_{t+\Delta t/2} \]
End Do

(Propagation of nuclear momentum by \( \Delta t/2 \))
\[ P_{t+\Delta t} = P_{t+\Delta t/2} - \frac{\Delta t}{2} \langle \hat{V}'(Q_{t+\Delta t}) \rangle \psi_{t+\Delta t}. \]
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