How important are the residual nonadiabatic couplings for an accurate simulation of the nonadiabatic quantum dynamics?

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Quasidiabatization of the molecular Hamiltonian is a standard approach to remove the singularity of nonadiabatic couplings at a conical intersection of adiabatic potential energy surfaces. Typically, the residual nonadiabatic couplings between quasidiabatic states are simply neglected. Here, we investigate the validity of this potentially drastic approximation by comparing the quantum dynamics simulated either with or without these couplings. By comparing the two simulations in the same quasidiabatic representation, we entirely avoid errors due to the transformation between representations. To eliminate grid and time discretization errors even in simulations with the nonseparable quasidiabatic Hamiltonian, we use the highly accurate and general eighth-order composition of the implicit midpoint method. To show that the importance of the residual couplings can depend on the employed quasidiabatization scheme, we compare the first- and second-order regular diabatizations applied to the cubic $E\otimes e$ Jahn–Teller model, whose parameters were chosen so that the magnitudes of the residual couplings differed by a factor of 200. As a consequence, neglecting the residual couplings in the first-order scheme results in very unreliable dynamics, while it has almost no effect in the second-order scheme. In contrast, the simulation with the exact quasidiabatic Hamiltonian is accurate regardless of the quasidiabatization scheme.

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I. INTRODUCTION

The celebrated Born–Oppenheimer approximation, which treats the electronic and nuclear motions in molecules separately, is no longer valid for describing processes involving two or more strongly vibronically coupled electronic states. A common approach that goes beyond this approximation consists in solving the time-dependent Schrödinger equation with a truncated molecular Hamiltonian that includes only a few, most significantly coupled Born–Oppenheimer electronic states. The “adiabatic” states, obtained directly from the electronic structure calculations, are, however, not adequate for representing the molecular Hamiltonian in the region of strong nonadiabatic couplings; in particular, the couplings between the states diverge to infinity at conical intersections, where potential energy surfaces of two or more adiabatic states intersect.

Quasidiabatization of the molecular Hamiltonian by a coordinate-dependent unitary transformation rectifies this singularity of the nonadiabatic couplings. The transformation matrix can be obtained by various quasidiabatization schemes, of which a few representative examples include the methods based on the integration of the nonadiabatic couplings or on different molecular properties and the block-diagonalization or regularized diabatization schemes. For more than one nuclear dimension, however, no quasidiabatization scheme leads to the strictly diabatic states, i.e., states in which the nonadiabatic couplings are eliminated completely, unless infinitely many electronic states are considered. In practice, it is, therefore, common to ignore the residual nonadiabatic couplings and thus obtain an approximate quasidiabatic Hamiltonian, which has a simpler, separable form convenient for quantum simulations.

To investigate the importance of the residual couplings for the accuracy of the dynamics, we compare nonadiabatic simulations performed either with the exact quasidiabatic Hamiltonian—obtained through an exact unitary transformation of the adiabatic Hamiltonian—or with the approximate quasidiabatic Hamiltonian, which neglects the residual couplings. The results obtained with the exact quasidiabatic Hamiltonian serve as the exact benchmark as long as the numerical errors are negligible. Therefore, for a valid comparison, one needs a time propagation scheme that can treat even the nonseparable exact quasidiabatic Hamiltonian and that ensures negligible numerical errors (in comparison to the errors due to neglecting the residual couplings). This consideration led us to choose the
optimal eighth-order\textsuperscript{11} composition\textsuperscript{15-18} of the implicit midpoint method,\textsuperscript{47-50} which satisfies both requirements and, moreover, preserves exactly geometric properties of the exact solution.\textsuperscript{47-50}

Although all quasidiabatization schemes remove the numerically problematic singularity of the nonadiabatic couplings, the magnitude of the residual couplings depends on the employed scheme.\textsuperscript{21} To find out how the errors due to ignoring the residual couplings depend on the sophistication of the quasidiabatization, we, therefore, compare the first- and second-order regularized diabatizations\textsuperscript{39-41} in the cubic $E \otimes e$ Jahn–Teller model, in which even the strictly diabatic Hamiltonian exists and both quasidiabatic and strictly diabatic Hamiltonians can be obtained analytically.

II. THEORY

We begin by introducing the standard molecular Hamiltonian $\mathcal{H} = \mathcal{T}_N + \mathcal{T}_e + \mathcal{V}$, where $\mathcal{T}_N$ and $\mathcal{T}_e$ are the kinetic energy operators of the nuclei and electrons, and $\mathcal{V}$ is the molecular potential energy operator. One may express the molecular Hamiltonian equivalently as $\mathcal{H} = \mathcal{T}_N + \mathcal{H}_e$ by defining the electronic Hamiltonian $\mathcal{H}_e := \mathcal{T}_e + \mathcal{V}$, an operator acting on the electronic degrees of freedom and depending parametrically on the nuclear coordinates described by a $D$-dimensional vector $Q$. For each fixed nuclear geometry, the time-independent Schrödinger equation $\mathcal{H}_e(Q)|n(Q)\rangle = V_n(Q)|n(Q)\rangle$ for $\mathcal{H}_e(Q)$ can be solved to obtain the $n$th adiabatic state $|n(Q)\rangle$ and potential energy surface $V_n(Q)$ for $n \in \mathbb{N}$.

These coordinate-dependent eigenstates $|n(Q)\rangle$ can be employed to expand the exact solution of the time-dependent molecular Schrödinger equation

\begin{equation}
\frac{i\hbar}{\partial t}|\Psi(Q,t)\rangle = \mathcal{H}|\Psi(Q,t)\rangle \tag{1}
\end{equation}

with Hamiltonian $\mathcal{H}$ as an infinite series

\begin{equation}
|\Psi(Q,t)\rangle_{\text{exact}} = \sum_{n=1}^{\infty} \psi_n^{\text{ad}}(Q,t)|n(Q)\rangle. \tag{2}
\end{equation}

Note that Eqs. (1) and (2) combine the coordinate representation for the nuclei with the representation-independent Dirac notation for the electronic states; $\psi_n^{\text{ad}}(Q,t)$ is the time-dependent nuclear wavefunction (a wavepacket) on the $n$th adiabatic electronic surface. The Born–Huang expansion\textsuperscript{52} of Eq. (2) is exact when an infinite number of electronic states are
included, but in practice, $|\Psi(Q,t)\rangle_{\text{exact}}$ is approximated by truncating the sum in Eq. (2) and including only the most important $S$ electronic states: 

$$
|\Psi(Q,t)\rangle_{\text{exact}} \approx |\Psi(Q,t)\rangle_{\text{trunc}} := \sum_{n=1}^{S} \psi_{n}^{\text{ad}}(Q,t)|n(Q)\rangle;
$$

for brevity, we shall omit the subscript “trunc” in $|\Psi(Q,t)\rangle_{\text{trunc}}$ from now on.

Substituting ansatz (3) into the time-dependent Schrödinger equation (1) and projecting onto states $\langle m(Q) |$ for $m \in \{1, \ldots, S\}$ leads to the ordinary differential equation

$$
i\hbar \frac{d}{dt} \psi_{n}^{\text{ad}}(t) = \hat{H}_{\text{ad}} \psi_{n}^{\text{ad}}(t),
$$

expressed in a compact, representation-independent matrix notation: **bold** font indicates either an $S \times S$ matrix (i.e., an electronic operator) or an $S$-dimensional vector, and the hat ^ denotes a nuclear operator. In particular, $\hat{H}_{\text{ad}}$ is the adiabatic Hamiltonian matrix with elements $(\hat{H}_{\text{ad}})_{mn} = \langle m|H|n\rangle$, and $\psi_{n}^{\text{ad}}(t)$ is the molecular wavepacket in the adiabatic representation with components $\psi_{n}^{\text{ad}}(t)$; henceforth, $m, n \in \{1, \ldots, S\}$ unless otherwise stated.

Assuming the standard form $\mathcal{T}_{N} = \hat{P}^2/2M$ of the nuclear kinetic energy operator, the adiabatic Hamiltonian matrix is given by the formula

$$
\hat{H}_{\text{ad}} = \frac{1}{2M} [\hat{P}^2 \mathbf{1} - 2i\hbar \mathbf{F}_{\text{ad}}(\hat{Q}) \cdot \hat{P} - \hbar^2 \mathbf{G}_{\text{ad}}(\hat{Q})] + \mathbf{V}_{\text{ad}}(\hat{Q}),
$$

which depends on the diagonal adiabatic potential energy matrix $[\mathbf{V}_{\text{ad}}(Q)]_{mn} := V_{n}(Q)\delta_{mn}$, the nonadiabatic vector couplings $[\mathbf{F}_{\text{ad}}(Q)]_{mn} := \langle m(Q)|\nabla n(Q)\rangle$, and the nonadiabatic scalar couplings $[\mathbf{G}_{\text{ad}}(Q)]_{mn} := \langle m(Q)|\nabla^2 n(Q)\rangle$. The dot · denotes the dot product in the $D$-dimensional nuclear vector space, and $P$ is the momentum conjugate to $Q$. Note that the coordinates are mass-scaled for simplicity.

The nonadiabatic vector couplings can be re-expressed using the Hellmann-Feynman theorem as

$$
[\mathbf{F}_{\text{ad}}(Q)]_{mn} = \frac{\langle m(Q)|\nabla \mathcal{H}_{e}(Q)|n(Q)\rangle}{V_{n}(Q) - V_{m}(Q)}, \quad m \neq n,
$$

accentuating the singularity of these couplings at a conical intersection—a nuclear geometry $Q = Q_0$ where $[\mathbf{V}_{\text{ad}}(Q_0)]_{m} = [\mathbf{V}_{\text{ad}}(Q_0)]_{n}$ for $m \neq n$. Another complication associated with conical intersections is the geometric phase effect: the sign change of the real-valued adiabatic electronic state $|n(Q)\rangle$ when transported along a loop containing a conical intersection. To avoid these issues, one can transform the adiabatic Hamiltonian
to the quasidiabatic basis

$$|n'(Q)⟩ = \sum_{m=1}^{S} |m(Q)⟩ [S(Q) †]_{mn}$$ (7)

and thus obtain the \textit{exact quasidiabatic Hamiltonian}

$$\hat{H}_{qd-exact} := S(\hat{Q}) \hat{H}_{ad} S(\hat{Q}) † = \frac{1}{2M} [\hat{P}^2 1 - 2i\hbar \mathbf{F}_{qd}(\hat{Q}) \cdot \hat{P} - \hbar^2 \mathbf{G}_{qd}(\hat{Q})] + \mathbf{V}_{qd}(\hat{Q}),$$ (8)

where $[\mathbf{V}_{qd}(Q)]_{mn} := \langle m'(Q)|\mathcal{H}_e(Q)|n'(Q)⟩$ is the nondiagonal quasidiabatic potential energy matrix, while $[\mathbf{F}_{qd}(Q)]_{mn} := \langle m'(Q)|\nabla n'(Q)⟩$ and $[\mathbf{G}_{qd}(Q)]_{mn} := \langle m'(Q)|\nabla^2 n'(Q)⟩$ are the residual vector and scalar couplings, respectively. The transformation matrix $S(Q)$ is obtained by any of the many quasidiabatization schemes, but the magnitude of the residual nonadiabatic couplings depends on the quasidiabatization scheme. Following Ref. [21] we measure this magnitude with the quantity

$$\mathcal{R} [\mathbf{F}_{qd}(Q)] := \int ||\mathbf{F}_{qd}(Q)||^2 dQ,$$ (9)

where

$$||\mathbf{F}_{qd}(Q)||^2 := \text{Tr}[\mathbf{F}_{qd}(Q) † \cdot \mathbf{F}_{qd}(Q)] = \text{Tr}[\sum_{l=1}^{D} \mathbf{F}_{qd}(Q) † l \mathbf{F}_{qd}(Q) l]$$ (10)

is the square of the Frobenius norm of $\mathbf{F}_{qd}(Q)$ [note that the evaluation of Eq. (10) involves both a product of $S \times S$ matrices and a scalar product of $D$-vectors]. Yet, it is well-known that, unless $S$ is infinite or $D = 1$, in general no diabatization scheme provides the strictly diabatic states [i.e., states in which the exact Hamiltonian (8) has zero residual nonadiabatic couplings]. The transformation by $S(Q)$ can only lead to quasidiabatic states, which are coupled both by the off-diagonal ($m \neq n$) elements of the quasidiabatic potential energy matrix $[\mathbf{V}_{qd}(Q)]_{mn}$ and by the perhaps small but nonvanishing residual nonadiabatic couplings. In practice, however, these residual couplings are often ignored in Eq. (8) in order to obtain the \textit{approximate quasidiabatic Hamiltonian}

$$\hat{H}_{qd-approx} := \frac{\hat{P}^2}{2M} 1 + \mathbf{V}_{qd}(\hat{Q}).$$ (11)
In what follows, we study the importance of the residual couplings in the cubic $E \otimes e$ Jahn–Teller model in which doubly degenerate electronic states labeled by $n = 1$ and $n = 2$ are coupled by doubly degenerate normal modes $Q_1$ and $Q_2$. Throughout the study, we work in natural units (n.u.) by setting $k = M = \hbar = 1$ n.u., where $M$ is the mass associated with the degenerate normal modes, and $\hbar \omega = \hbar \sqrt{k/M}$ is a quantum of the vibrational energy of these modes. Moreover, we express the potential energy surface in polar coordinates: the radius $\rho(Q) := \sqrt{Q_1^2 + Q_2^2}$ and polar angle $\phi(Q) := \arctan (Q_2/Q_1)$.

Although the strictly diabatic Hamiltonian

\[
\hat{H}_{\text{diab}} = \hat{\mathbf{p}}^2/2M + V_{\text{diab}}(\hat{\mathbf{Q}}) \tag{12}
\]

does not exist in general, it can exist exceptionally and, in fact, is used to define the Jahn–Teller model. In Eq. (12), the diabatic potential energy matrix

\[
V_{\text{diab}}(Q) = \begin{pmatrix}
E_0(Q) & E_{\text{cpl}}(Q) e^{-2i\theta(Q)} \\
E_{\text{cpl}}(Q) e^{2i\theta(Q)} & E_0(Q)
\end{pmatrix} \tag{13}
\]

depends on the harmonic potential energy $E_0(Q) := k\rho(Q)^2/2$, Jahn–Teller coupling $E_{\text{cpl}}(Q) := \rho(Q)[f(Q)+2c_2h(Q) + (c_2^2 + 2c_1c_3)\rho(Q)^2]^{1/2}$, and mixing angle

\[
\theta(Q) := \frac{1}{2} \arctan \frac{g(Q) \sin \phi(Q) - c_2 \rho(Q)^2 \sin 2\phi(Q)}{g(Q) \cos \phi(Q) + c_2 \rho(Q)^2 \cos 2\phi(Q)}. \tag{15}
\]

Functions $f(Q) := c_2^2 + c_2^3 \rho(Q)^4$, $g(Q) := c_1 \rho(Q) + c_3 \rho(Q)^2$, and $h(Q) := g(Q) \cos 3\phi(Q)$ were defined in order to simplify expressions (14) and (15); we chose the values of the Jahn–Teller coupling coefficients $c_1 = 0.8$ n.u., $c_2 = 0.04$ n.u., and $c_3 = 0.001$ n.u. so that $c_1 \gg c_2 \gg c_3$.

The adiabatic states in the Jahn–Teller model are obtained by a process inverse to diabatization, i.e., by a unitary transformation of the strictly diabatic states using any matrix that diagonalizes $V_{\text{diab}}(Q)$. Following Refs. 39 and 66, we employed the transformation matrix

\[
T(Q) = \frac{1}{\sqrt{2}} \begin{pmatrix}
e^{-i\theta(Q)} & e^{-i\theta(Q)} \\
e^{i\theta(Q)} & -e^{i\theta(Q)}
\end{pmatrix} \tag{16}
\]

In the resulting adiabatic representation, the diagonal potential energy matrix has elements $V_1(Q) = V_+(Q)$ and $V_2(Q) = V_-(Q)$, where $V_\pm(Q) := E_0(Q) \pm E_{\text{cpl}}(Q)$. [Elements of $V_{\text{ad}}(Q)$}
and $V_{\text{dih}}(Q)$ are plotted in Fig. 1. Transformation (16) yields also analytical expressions for the nonadiabatic vector couplings:

$$F_{\text{ad}}(Q) = -i \nabla \theta(Q) \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

(17)

and for the nonadiabatic scalar couplings

$$G_{\text{ad}}(Q) = -i \nabla^2 \theta(Q) \begin{pmatrix} [\nabla \theta(Q)]^2 & i \nabla^2 \theta(Q) \\ i \nabla^2 \theta(Q) & [\nabla \theta(Q)]^2 \end{pmatrix}.$$  

(18)

As expected, the nonadiabatic couplings diverge to infinity at the conical intersection $\rho(Q) = 0$ since

$$\frac{\partial \theta}{\partial \phi} = \frac{f(Q) - 2\rho(Q)^2(c_2^2 - c_1c_3) - c_2h(Q)}{\rho(Q)[f(Q) + \rho(Q)^2(c_2^2 + 2c_1c_3) + 2c_2h(Q)]} \xrightarrow{\rho \to 0} \infty. $$

(19)

In the cubic Jahn–Teller model, the regularized diabatization scheme can be implemented analytically; the $j$th-order adiabatic to quasidiabatic transformation matrix

$$S^{(j)}(Q) = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{-i\theta^{(j)}(Q)} & e^{-i\theta^{(j)}(Q)} \\ e^{i\theta^{(j)}(Q)} & -e^{i\theta^{(j)}(Q)} \end{pmatrix}$$

(20)

is, for $j \in \{1, 2\}$, obtained simply by replacing $\theta(Q)$ with $\theta^{(j)}(Q)$ in Eq. (16) for $T(Q)$. In Eq. (20), $\theta^{(1)}(Q) := \phi(Q)/2$ and

$$\theta^{(2)}(Q) = \frac{1}{2} \arctan \frac{c_1\rho(Q) \sin \phi(Q) - c_2\rho(Q)^2 \sin 2\phi(Q)}{c_1\rho(Q) \cos \phi(Q) + c_2\rho(Q)^2 \cos 2\phi(Q)}. $$

(21)

Note that it is not meaningful to define higher-order quasidiabatization schemes because $\theta^{(3)}(Q) = \theta(Q)$, i.e., the third-order quasidiabatization of the cubic Jahn–Teller model is already identical to the strict diabatization. The first-order ($j = 1$) and second-order ($j = 2$) quasidiabatizations yield the potential energy matrices

$$V_{\text{qd}}^{(j)}(Q) := S^{(j)}(Q) V_{\text{ad}}(Q) S^{(j)}(Q)^\dagger = \begin{pmatrix} E_0(Q) & E_{\text{cpl}}(Q)e^{-2i\theta^{(j)}(Q)} \\ E_{\text{cpl}}(Q)e^{2i\theta^{(j)}(Q)} & E_0(Q) \end{pmatrix}, $$

(22)

the residual vector couplings

$$F_{\text{qd}}^{(j)}(Q) := S^{(j)}(Q) F_{\text{ad}}(Q) S^{(j)}(Q)^\dagger + S^{(j)}(Q) \nabla S^{(j)}(Q)^\dagger
= -i \nabla \theta^{(j)}(Q) \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, $$

(23)
FIG. 1. Potential energy surfaces in the cubic $E \otimes e$ Jahn–Teller model in the vicinity of the conical intersection at $Q = 0$. (a) Elements $V_1(Q) = V_+(Q)$ (red) and $V_2(Q) = V_-(Q)$ (blue) of the diagonal adiabatic potential energy matrix; the two surfaces intersect (touch) at the point $Q = 0$. The diabatic potential energy matrix in the Jahn–Teller model consists of (b) the harmonic potential energy surfaces $E_0(Q)$ on the diagonal and (c) the off-diagonal complex couplings of magnitude $E_{cpl}(Q)$.

and the residual scalar couplings

$$G_{qd}^{(j)}(Q) := S^{(j)}(Q) G_{ad}(Q) S^{(j)}(Q)$$

$$+ 2 S^{(j)}(Q) F_{ad}(Q) \nabla S^{(j)}(Q) + S^{(j)}(Q) \nabla^2 S^{(j)}(Q)$$

$$= -i \nabla^2 \theta_-(Q) \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} - [\nabla \theta_-(Q)]^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix},$$

(24)

where $\theta_-(Q) := \theta(Q) - \theta^{(j)}(Q)$.

Although both quasidiabatization schemes remove the singularity of the nonadiabatic couplings, we have chosen the Jahn–Teller coupling coefficients so that $c_1 \gg c_2 \gg c_3$ and, as a consequence, the magnitude $R[F_{qd}^{(1)}(Q)] = 0.6$ n.u. of the residual couplings obtained from the first-order scheme is much larger than the corresponding magnitude $R[F_{qd}^{(2)}(Q)] = 0.003$ n.u. for the second-order scheme. The values of $R[F_{qd}^{(1)}(Q)]$ and
$R|F^{(2)}_{qd}(Q)|$ were evaluated on a uniform grid of $32 \times 32$ points defined between $Q_l = -7$ n.u. and $Q_l = 7$ n.u. for $l \in \{1, 2\}$; the same grid was used for the numerical propagation of the wavepackets. To evaluate how nonadiabatic simulations are affected by ignoring the residual couplings $F^{(j)}_{qd}(Q)$, we simulated—with either the exact or approximate quasidiabatic Hamiltonian—the quantum dynamics following a transition from the ground vibrational eigenstate of $V_A(Q) = -E_{\text{gap}} + E_0(Q)$, which is not explicitly a part of the model, to the degenerate states of the Jahn–Teller model. Invoking the time-dependent perturbation theory and Condon approximation, we considered the initial state in the quasidiabatic representation to be
\[
\psi(0) := \frac{e^{-\rho(Q)^2/2\hbar}}{\sqrt{2\pi\hbar}} \begin{pmatrix} 1 \\ 1 \end{pmatrix};
\]
we omit the superscript “qd” on wavepackets for brevity.

The influence of the residual nonadiabatic couplings on the accuracy was measured with the quantum fidelity
\[ F^{(j)}(t) := |\langle \psi^{(j)}_{qd-approx}(t)|\psi^{(j)}_{qd-exact}(t)\rangle|^2 \]
and distance
\[ D^{(j)}(t) := \|\psi^{(j)}_{qd-approx}(t) - \psi^{(j)}_{qd-exact}(t)\| \]
between the states $\psi^{(j)}_{qd-approx}(t)$ and $\psi^{(j)}_{qd-exact}(t)$, evolved with the approximate and exact quasidiabatic Hamiltonians, respectively. [I.e., $\psi^{(j)}_i(t) = \exp(-i\hat{H}_i t/\hbar)\psi(0)$ for $i \in \{qd-approx, qd-exact\}$, and $j \in \{1, 2\}$.] Wavepacket $\psi^{(j)}_{qd-exact}(t)$ serves as the exact benchmark because it is numerically converged in both grid and time (see Sec. S2 of the supplementary material) and because the exact quasidiabatic and adiabatic Hamiltonians are exact unitary transformations of each other. In fact, our previous study\textsuperscript{43} on a similar system showed that the exact quasidiabatic and strictly diabatic Hamiltonians yield nearly identical numerical results. Here, however, we intentionally avoid using the strictly diabatic Hamiltonian as a benchmark and use it only to define the model, in order that the approach and conclusions of this study are applicable also to realistic systems, where the strictly diabatic Hamiltonians do not exist.\textsuperscript{21,42} Moreover, by both propagating and comparing the wavepackets in the same quasidiabatic representation, we avoided contaminating the errors due to the neglect of the residual couplings with the errors due to the transformation between representations.

The exact quasidiabatic Hamiltonian [in Eq. (8)] cannot be expressed as a sum of terms depending purely on either the position or momentum operator. Due to this nonseparable nature of the Hamiltonian, we required an integrator that is applicable regardless of the form of the Hamiltonian. For example, the popular split-operator method\textsuperscript{48,71–73} could not
be employed. The wavepackets were, therefore, propagated with the composition of the implicit midpoint method, which, like the closely related trapezoidal rule (Crank–Nicolson method), works for both separable and nonseparable Hamiltonians, as long as the action of the Hamiltonian on the wavepacket can be evaluated.

The hermiticity of Hamiltonian (8) is broken on a finite grid because the commutator relation \([ \hat{P}, \mathbf{F}_{qd}(\hat{Q}) ] = -i\hbar \nabla \cdot \mathbf{F}_{qd}(\hat{Q}) \) only holds approximately unless the grid is infinitely dense. However, the norm conservation, which relies on the hermiticity of the Hamiltonian, is important for \( \mathcal{F}^{(j)}(t) \) and \( \mathcal{D}^{(j)}(t) \) to be valid measures of the importance of the residual nonadiabatic couplings. To make the exact quasidiabatic Hamiltonian exactly Hermitian, we re-express Hamiltonian (8) as

\[
\hat{H}_{qd-exact}^{(j)} = \frac{1}{2M} [ \hat{P} \mathbf{1} - i\hbar \mathbf{F}_{qd}^{(j)}(\hat{Q}) ]^2 + V_{qd}^{(j)}(\hat{Q}),
\]

using the relationship

\[
\mathbf{G}_{qd}^{(j)}(Q) = \nabla \cdot \mathbf{F}_{qd}^{(j)}(Q) + \mathbf{F}_{qd}^{(j)}(Q)^2,
\]

which holds—exceptionally—for systems, such as the Jahn–Teller model, that can be represented exactly by a finite number of states; in general, Eq. (27) only holds when \( S \to \infty \).

When the hermiticity of the Hamiltonian is ensured, the norm is conserved exactly (see Sec. S1 of the supplementary material) because the implicit midpoint method, which we employed for the time propagation, exactly conserves the norm along with other geometric properties: energy, linearity, inner product, symplecticity, stability, symmetry, and time reversibility (see Ref. 51).

For a valid comparison of the two wavepackets propagated with either the exact or approximate quasidiabatic Hamiltonian, the spatial and time discretization errors must be much smaller than the errors due to omitting the residual couplings. Owing to its exact symmetry, the implicit midpoint method can be composed using various schemes to obtain integrators of arbitrary even orders of accuracy in the time step; we composed the implicit midpoint method according to the optimal scheme to obtain an eighth-order integrator. By using this high-order integrator with a small time step of \( \Delta t = 1/(40\omega) = 0.025 \) n.u., the time discretization errors were kept minuscule (see Sec. S2 of the supplementary material). In Sec. S2 of the supplementary material, we also show that the grid discretization errors were negligible.
FIG. 2. Comparison of the power spectra obtained by Fourier transforming the damped autocorrelation function obtained with either the exact \((i = qd\text{-exact})\) or approximate \((i = qd\text{-approx})\) quasidiabatic Hamiltonian for the (a) first-order \((j = 1)\) and (b) second-order \((j = 2)\) quasidiabatization schemes. The autocorrelation function \(C_i^{(j)}(t) = \langle \psi(0)|\psi_i^{(j)}(t) \rangle\) was multiplied by the damping function \(d(t) = \exp\left[(-t/t_{\text{damp}})^2\right]\) with \(t_{\text{damp}} = 50\) n.u. to emulate the broadening of the spectral peaks.

III. RESULTS AND DISCUSSION

First, we study the impact of neglecting the residual couplings on the power spectrum \(I(\omega)\) (Fig. 2), potential energy \(\langle V_{qd}(t)\rangle\) (Fig. 3), and position \(\langle \rho(t) \rangle\) (Fig. 4). We omit the quasidiabatic populations, which remain constant at their initial values of \(1/2\) due to the symmetry of the quasidiabatic Jahn–Teller Hamiltonian around the conical intersection at which the initial Gaussian wavepacket was placed.

Figure 2 shows that the power spectrum is accurate regardless of whether the residual couplings are included in the Hamiltonian. Even the least accurate spectrum, obtained with the approximate first-order quasidiabatic Hamiltonian \((i = qd\text{-approx}, j = 1)\), differs very little from the exact spectrum (obtained with the exact first-order quasidiabatic Hamiltonian); these tiny differences are only visible in the zoomed-in version [see inset of Fig. 2(a)]. In contrast, panels (a) of Figs. 3 and 4 show that, already after \(t \approx 50\) n.u., the accuracies of both the potential energy \(\langle V_{qd}\rangle^{(1)}(t)\) and position \(\langle \rho \rangle^{(1)}(t)\) are affected significantly by neglecting the residual couplings when the first-order \((j = 1)\) quasidiabatization scheme is employed.

This is even more clearly demonstrated by comparing the error \(|\Delta A(t)| := |A_{qd\text{-approx}}(t) - A_{qd\text{-exact}}(t)|\) of an observable with its range \(R_A := A_{\text{max}} - A_{\text{min}}\), where \(A_{\text{max}}\) and \(A_{\text{min}}\) are
FIG. 3. Comparison of the potential energy, \( \langle V_{qd}\rangle_{i}^{(j)}(t) := \langle \psi_{i}^{(j)}(t)|V_{qd}(\hat{Q})|\psi_{i}^{(j)}(t) \rangle \), obtained with either the exact \((i = qd-exact)\) or approximate \((i = qd-approx)\) quasidiabatic Hamiltonian for the (a) first-order \((j = 1)\) and (b) second-order \((j = 2)\) quasidiabatization schemes. The exact energy conservation by the implicit midpoint method (see Sec. S1 of the supplementary material) implies that the kinetic energy satisfies the relation

\[
\langle T_{qd}\rangle_{i}^{(j)}(t) = \langle E(0)\rangle_{i}^{(j)} - \langle V_{qd}\rangle_{i}^{(j)}(t),
\]

where \(\langle E(t)\rangle := \langle \psi_{i}^{(j)}(t)|\hat{H}_{i}^{(j)}|\psi_{i}^{(j)}(t) \rangle = 1\) n.u. for all times \(t\).

FIG. 4. Comparison of the position, \(\langle \rho \rangle_{i}^{(j)}(t) := \left[ \sum_{l=1}^{2} \langle \psi_{i}^{(j)}(t)|\hat{Q}_{l}|\psi_{i}^{(j)}(t) \rangle^{2} \right]^{1/2}\), obtained with either the exact \((i = qd-exact)\) or approximate \((i = qd-approx)\) quasidiabatic Hamiltonian for the (a) first-order \((j = 1)\) and (b) second-order \((j = 2)\) quasidiabatization schemes.

The maximum and minimum values of \(A_{qd-exact}(t)\) over the time interval \(0 \leq t \leq t_f = 175\) n.u. If the first-order scheme is used, then the potential energy and position obtained with the approximate quasidiabatic Hamiltonian cannot be trusted because, e.g., at \(t = 160\) n.u., \(|\Delta \langle V_{qd}\rangle^{(1)}(t)\rangle)_{i}^{(1)} = 0.65\) and, at \(t = 168\) n.u., \(|\Delta \langle \rho \rangle^{(1)}(t)\rangle)_{i}^{(1)} = 0.45\). Yet, both the potential energy \(\langle V_{qd}\rangle^{(2)}(t)\) and position \(\langle \rho \rangle^{(2)}(t)\) are obtained accurately until the final time \(t = t_f\) regardless of the inclusion of the residual couplings when the second-order quasidiabatization scheme is employed [see panels (b) of Figs. 3 and 4 and Sec. S2 of the
FIG. 5. Comparison of the wavepackets propagated with either the exact (i = qd-exact) or approximate (i = qd-approx) quasidiabatic Hamiltonian obtained by the first-order [j = 1, panels (a)–(b)] and second-order [j = 2, panels (c)–(d)] quasidiabatization schemes. [Only the real part of the nuclear wavepacket in the second (n = 2) electronic state is shown.]

While some observables, such as the spectrum, may be accurately computed even from a rather poor wavepacket, an accurate wavepacket dynamics ensures the accuracy of all observables (except some very pathological ones). Therefore, we directly compare the wavepackets at the final time $t = t_f = 175$ n.u. Figure 5 shows that, on one hand, the wavepacket propagated with the second-order quasidiabatic Hamiltonian is accurate even when the residual couplings are neglected [compare panels (c) and (d)]. On the other hand, $\psi_{qd-approx}^{(1)}(t_f)$, propagated with the approximate first-order quasidiabatic Hamiltonian, has a similar overall shape to $\psi_{qd-exact}^{(1)}(t_f)$, but differs significantly in the nodal structure and other details [compare panels (a) and (b)].

For a quantitative measure of the impact of the residual couplings on the propagated wavepacket, we also analyze the quantum fidelity $F^{(j)}(t) \in [0, 1]$ and distance $D^{(j)}(t) \in [0, 2]$ between $\psi_{qd-approx}^{(j)}(t)$ and $\psi_{qd-exact}^{(j)}(t)$. The more important the residual couplings, the smaller the quantum fidelity $F^{(j)}(t)$ and the larger the distance $D^{(j)}(t)$. Figure 6 reaffirms that ignoring the residual couplings is detrimental in the first-order (j = 1) scheme, in which the fidelity decreases to $F^{(1)}(t_f) \approx 0.6$ and the distance increases to $D^{(1)}(t_f) \approx 0.6$. In contrast, both fidelity $F^{(2)}(t)$ and distance $D^{(2)}(t)$ remain close to their initial values during the whole simulation if the Hamiltonian is quasidiabatized using the second-order scheme.

supplementary material; $|\Delta \langle V_{qd} \rangle^{(2)}(t) |/R_{\langle V_{qd} \rangle^{(2)}(2)} \leq 0.004$, $|\Delta \langle \rho \rangle^{(2)}(t) |/R_{\langle \rho \rangle^{(2)}(2)} \leq 0.003$. 
FIG. 6. Importance of the residual nonadiabatic couplings for the accuracy of the propagated wavepacket is measured by the (a) quantum fidelity $F^{(j)}(t)$ and (b) distance $D^{(j)}(t)$ between the wavepackets propagated with either the exact or approximate quasidiabatic Hamiltonian obtained by the first-order $(j = 1)$ and second-order $(j = 2)$ quasidiabatization schemes.

IV. CONCLUSION

Quasidiabatizing the adiabatic states removes the problematic singularity of the nonadiabatic couplings at the conical intersection. However, in realistic chemical systems, no quasidiabatization scheme can completely remove the couplings between the electronic states unless infinitely many states are considered.

Still, the nonvanishing couplings between the quasidiabatic states are often neglected. Returning to the question posed in the title, the magnitude and, therefore, the importance of these neglected residual nonadiabatic couplings depends essentially on the employed quasidiabatization scheme. To demonstrate this, we chose an example in which ignoring the residual couplings affected substantially the accuracy of the quantum dynamics simulation based on the simple, first-order quasidiabatization scheme but not when the second-order scheme was employed.

In the cubic $E \otimes e$ Jahn–Teller model, the implementation of the more sophisticated second-order scheme was still feasible but the implementation of sophisticated quasidiabatization schemes, which lead to negligible residual couplings, would be more challenging in more complex systems. In such situations, it would be particularly beneficial to propagate the wavepacket with the exact quasidiabatic Hamiltonian, which is accurate regardless of the employed quasidiabatization scheme (as shown in Sec. S2 of the supplementary material and in Ref. [43]). Although the nonseparable form of this Hamiltonian complicates the time propagation, there exist efficient geometric integrators, such as the high-order compositions of the implicit midpoint method, that are applicable even to such Hamiltonians. Lastly,
accurately propagating the wavepacket with the exact quasidiabatic Hamiltonian would be crucial for establishing highly accurate benchmarks in unfamiliar systems, where the impact of the residual nonadiabatic couplings on the quantum dynamics simulations is not yet known.

SUPPLEMENTARY MATERIAL

See the supplementary material for the conservation of geometric properties by the implicit midpoint method and for the spatial and time discretization errors of the wavepacket and presented observables.

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DATA AVAILABILITY

The data that support the findings of this study are contained in the paper and the supplementary material.

Supplementary material for: How important are the residual nonadiabatic couplings for an accurate simulation of the nonadiabatic quantum dynamics?

S1. CONSERVATION OF GEOMETRIC PROPERTIES BY THE IMPLICIT MIDPOINT METHOD

We demonstrate the conservation of the wavepacket’s norm \(\|\psi(t)\|\) and energy \(\langle E(t) \rangle\) by the optimal eighth-order\(^{[44]}\) composition\(^{[45-48]}\) of the implicit midpoint method. Figure S1 shows that both the norm and energy are conserved to machine precision \(< 10^{-14}\). In
FIG. S1. Exact conservation of geometric properties by the employed integrator: the conservation of the norm $\|\psi_i^{(j)}(t)\|$ [panels (a)–(b)] and energy $\langle E(t) \rangle_i^{(j)}$ [panels (c)–(d)] of the wavepacket propagated with either the exact ($i = \text{qd-exact}$) or approximate ($i = \text{qd-approx}$) quasidiabatic Hamiltonian obtained from either the first-order [$j = 1$, panels (a), (c)] or second-order [$j = 2$, panels (b), (d)] scheme. The initial values are $\|\psi_i^{(j)}(0)\| = 1$ for the norm and $\langle E(0) \rangle_i^{(j)} = 1$ n.u. for the energy.

In fact, they are conserved to machine precision regardless of the size of the time step (not shown). We refer the reader to Ref. 51 and the references therein for the analytical proof and numerical demonstration of the preservation of geometric properties of the exact solution (the conservation of norm, energy, and inner product, linearity, symplecticity, stability, symmetry, and time reversibility) by the compositions of the implicit midpoint method.

S2. SPATIAL AND TIME DISCRETIZATION ERRORS

For the comparisons presented in Figs. 2–6 of the main text to be valid, both the spatial and time discretization errors should be negligible to the errors due to the neglect of the residual nonadiabatic couplings. We used distance functionals $\epsilon^{\text{grid}}_N[\psi(t)] := \|\psi^{(\Delta t,N)}(t) - \psi^{(\Delta t,2N)}(t)\|$ and $\epsilon^{\text{time}}_{\Delta t}[\psi(t)] := \|\psi^{(\Delta t,N)}(t) - \psi^{(\Delta t/2,N)}(t)\|$ to measure the spatial and time discretization errors of $\psi^{(\Delta t,N)}(t)$, which denotes the molecular wavepacket propagated to time $t$ with the time step of $\Delta t = 0.025$ n.u. on a grid of $N \times N = 32 \times 32$ points. Similarly, we used $\epsilon^{\text{time}}_{\Delta t}(A) := |A^{(\Delta t,N)} - A^{(\Delta t/2,N)}|$ and $\epsilon^{\text{grid}}_N(A) := |A^{(\Delta t,N)} - A^{(\Delta t,2N)}|$ to measure the spatial and time discretization errors of $A^{(\Delta t,N)}$, an observable $A$ obtained from a simulation on a grid of $N \times N$ points with the time step $\Delta t$. The grid of $2N \times 2N$ points was defined so that it was both denser and wider by a factor of $\sqrt{2}$ (both in position and momentum...
FIG. S2. Grid discretization errors of the power spectrum $I^{(j)}_i(\omega)$ (shown in Fig. 2 of the main text) obtained from either the exact or approximate quasidiabatic Hamiltonian; the quasidiabatization was performed with either the first-order [$j = 1$, panels (a)–(b)] or second-order [$j = 2$, panels (c)–(d)] scheme. The errors $|\Delta I^{(j)}_i(\omega)|$ of the power spectrum due to ignoring the residual couplings are shown in gray for comparison. The nearly invisible errors in the left hand side panels are presented in log-scale in the right hand side panels.

Figures S2–S5 show that the grid discretization errors of every quantity presented in Figs. 2–6 of the main text are negligible to the errors due to the neglect of the residual nonadiabatic couplings regardless of the employed quasidiabatization scheme. Moreover, thanks to the high order of accuracy of the employed time propagation scheme, the time discretization errors of the quantities presented in Figs. 2–6 of the main text are even smaller than the corresponding spatial discretization errors (see Fig. S6). The small numerical errors of the wavepackets propagated with the exact quasidiabatic Hamiltonian validate them as the reference benchmark wavepackets because the exact quasidiabatic Hamiltonian is exact in the sense that it is a coordinate-dependent unitary transform of the adiabatic Hamiltonian.
FIG. S3. Grid discretization errors of the potential energy $\langle V_{q_d} \rangle^{(j)}(t)$ (shown in Fig. 3 of the main text). Line labels and the panel layout are analogous to Fig. S2.

FIG. S4. Grid discretization errors of the position $\langle \rho \rangle^{(j)}(t)$ (shown in Fig. 4 of the main text). Line labels and the panel layout are analogous to Fig. S2.
FIG. S5. Grid discretization errors of the wavepacket $\psi^{(j)}_i(t)$ propagated with either the exact or approximate quasidiabatic Hamiltonian compared with $\mathcal{D}^{(j)}(t)$, which measures the errors of the wavepacket due to ignoring the residual couplings; the quasidiabatization was performed with either the first-order [$j = 1$, panels (a)–(b)] or second-order [$j = 2$, panels (c)–(d)] scheme. The nearly invisible errors in the left hand side panels are presented in log-scale in the right hand side panels.

FIG. S6. Negligible time discretization errors ($\epsilon = \epsilon^{(\text{time})}_{\Delta t}$) of the (a) spectrum, (b) potential energy, and (c) position (the three observables presented in Figs. 2–4 of the main text), and of (d) the wavepacket $\psi^{(j)}_i(t)$ propagated with either the exact ($i = \text{qd-exact}$) or approximate ($i = \text{qd-approx}$) quasidiabatic Hamiltonian obtained with either the first-order ($j = 1$) or second-order ($j = 2$) quasidiabatization scheme.
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