Laser-induced electron localization in $\text{H}^+$: Mixed quantum-classical dynamics based on the exact time-dependent potential energy surface

Yasumitsu Suzuki, Ali Abedi, Neepa T. Maitra, and E.K.U. Gross

1Max-Planck Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany
2Department of Physics and Astronomy, Hunter College and the City University of New York, 695 Park Avenue, New York, New York 10065, USA
3European Theoretical Spectroscopy Facility (ETSF)

(Dated: June 15, 2015)

We study the exact nuclear time-dependent potential energy surface (TDPES) for laser-induced electron localization with a view to eventually developing a mixed quantum-classical dynamics method for strong-field processes. The TDPES is defined within the framework of the exact factorization [A. Abedi, N. T. Maitra, and E. K. U. Gross, Phys. Rev. Lett. 105, 123002 (2010)] and contains the exact effect of the couplings to the electronic subsystem and to any external fields within a scalar potential. We compare its features with those of the quasistatic potential energy surfaces (QSPES) often used to analyse strong-field processes. We show that the gauge-independent component of the TDPES has a mean-field-like character very close to the density-weighted average of the QSPESs. Oscillations in this component are smoothed out by the gauge-dependent component, and both components are needed to yield the correct force on the nuclei. Once the localization begins to set in, the gradient of the exact TDPES tracks one QSPES and then switches to the other, similar to the description provided by surface-hopping between QSPESs. We show that evolving an ensemble of classical nuclear trajectories on the exact TDPES accurately reproduces the exact dynamics. This study suggests that the mixed quantum-classical dynamics scheme based on evolving multiple classical nuclear trajectories on the exact TDPES will be a novel and useful method to simulate strong field processes.

PACS numbers: 31.15-p, 31.50.-x, 33.80.-t, 42.50.Hz, 82.20.-w

I. INTRODUCTION

With the advent of attosecond technology [1–4], the experimentally accessible time-scale has shifted to that of electronic motion. It allows the observation of electronic motion in real-time, and even offers the control of electron motion and localization via lasers. Several groups [7–26] have demonstrated that it is possible to control electronic motion in a dissociating molecule and localize it selectively on one of the products of dissociation, with several different strategies. One technique employs the carrier envelope phase (CEP) of a single few-cycle laser pulse [18–25], and another employs the time-delay between two coherent ultrashort pulses [7–17].

These experiments so far treat small systems (such as $\text{H}_2$ and $\text{D}_2$), with the aim of understanding the mechanisms of localization, before applying the techniques to the control of larger systems [27, 28]. Theoretical studies have a dual role [7, 26]: (i) to help understand the complex correlation between the electronic and nuclear dynamics, and (ii) to establish methods, generally extendable to larger systems, that accurately simulate the coupled electron-nuclear dynamics. For systems with more than two or three degrees of freedom, we must rely on approximate methods, and usually some kind of mixed quantum-classical approach is appropriate, where the electrons are treated quantum-mechanically, coupled to nuclei described via classical trajectories [29–32]. Different mixed quantum-classical schemes such as Ehrenfest and surface-hopping [33–35], differ in their treatment of the classical nuclear motion, but use the same form for the potential acting on the electrons. For dynamics in strong fields, a surface-hopping scheme between quasi-static potential energy surfaces (QSPES) was introduced [36–38], and in fact applied to the electron-localization problem [13]. Although this semiclassical approach was shown to reproduce the experimental asymmetries reasonably well, it is not altogether clear why surface-hopping should give good predictions, given its problems associated with over-coherence [39–46].

In this paper, we will study the possibility of using a potential derived from first-principles, the time-dependent potential energy surface (TDPES) [47, 48], in a mixed quantum-classical description of the coupled dynamics. This potential arises out of the exact factorization framework where a time-dependent Schrödinger equation (TDSE) for the nuclei alone can be formulated. The potentials appearing in this equation capture exactly all coupling to the electronic system as well as any external fields, and the resulting nuclear wavefunction reproduces the exact nuclear dynamics. The scalar potential is denoted the TDPES, and in many
situations, including all one-dimension problems, the 
TDPES is the only potential acting on the nuclear sub-
system; its gradient therefore yields the exact force on 
the nuclei. For this reason, it is important to gain an un-
derstanding of its structure, to address both points (i) 
and (ii) above. Therefore, our aim in this paper is to 
find the exact TDPES for the problem of laser-induced 
electron localization in a one-dimensional model of \( \text{H}_2^+ \), 
compare its structure with potential surfaces more tradi-
tionally used for strong-field dynamics, and study clas-
cial nuclear dynamics on the exact TDPES with a view 
to developing mixed quantum-classical schemes based 
on the exact factorization.

Previous work \( [49, 51] \) has analysed the structure of 
the exact TDPES for a case of field-free dynamics, non-
adibatic charge-transfer in the Shin-Metiu model \( [52] \), 
finding that much intuition is gained by analysing it 
in term of the Born-Oppenheimer (BO) potential en-
ergy surfaces (BOPESs), and that such an analysis en-
ables connections to be made with traditional approxi-
mate methods for coupled electron-ion dynamics, such 
as surface-hopping. Further, it was found that evolving 
an ensemble of classical nuclear trajectories on the exact 
TDPES accurately reproduces the exact nuclear dynam-
ic.

We will show here that analogous conclusions can be 
drawn for the laser-induced electron localization prob-
lem: an ensemble of classical nuclear trajectories evolv-
ing on the exact TDPES accurately reproduces the exact 
nuclear dynamics, and analysis in terms of the QSPESs, 
which play the role of the BOPESs when strong fields 
are present, is helpful. The TDPES naturally separates 
into a gauge-independent part and a gauge-dependent 
part. We show that the density-weighted average of 
the QSPESs approximates the gauge-independent com-
ponent, which is rather oscillatory and the force on the 
nuclei resulting from its gradient is incorrect. Once the 
gauge-dependent component of the TDPES is included, 
the oscillations smoothen out: together, they yield the 
correct force on the nuclei. Further, we find that, once 
localization begins to set in, the gradient of the exact TDPES 
at the location of the mean nuclear position, tracks 
that of one QSPES and then switches to the other, resem-
bling the picture provided by the semiclassical surface-
hopping approach \( [13, 37, 38] \).

A multiple trajectory Ehrenfest dynamics simulation 
shows that although the nuclear dynamics is reasonably 
reproduced, an incorrect electron localization asymme-
try is obtained. The error can be related to the incor-
cr bo projections of the electronic wavefunction. The 
act that the Ehrenfest dynamics yields inaccurate elec-
tron dynamics can be anticipated from our recent work 
on the exact electronic-TDPES \( [53] \); in this complemen-
tary picture, instead of asking what is the exact potential 
aacting on nuclei in an exact TDSE for nuclei, one asks 
what is the exact potential acting on electrons in an ex-
tTDSE for the electronic subsystem. We found \( [53] \) that the exact electronic-TDPES is significantly differ-
ent from the potential acting on electrons in the usual 
mixed quantum-classical schemes – including Ehrenfest 
as well as surface-hopping schemes – yielding signifi-
cant errors in the prediction of the electron localization 
asymmetry. The results of the present paper suggest 
that, instead, mixed quantum-classical schemes based 
on evolving multiple classical trajectories on the exact 
TDPES (or good approximations to it) will be a useful 
method to simulate strong field processes.

This paper is organized as follows. In section II, we 
review two different concepts of potential energy sur-
faces for TD processes in laser fields: the QSPES and the 
extact TDPES. In section III we compare the features of 
these potentials for electron localization dynamics in the 
dissociation of a model \( \text{H}_2^+ \) molecule induced by time-
delayed coherent ultra shortlaser pulses. We show the 
extact TDPES gives the correct force acting on nuclei, so 
evolving multiple classical trajectories on it reproduces 
the correct nuclear wavepacket dynamics. The force ob-
tained from surface-hopping between QSPESs can ap-
approximately reproduce such an exact force once local-
ization begins to set in. We also compute multiple tra-
jectory Ehrenfest dynamics and reveal how it fails to re-
produce electron localization dynamics while it reason-
ably reproduces the nuclear dynamics. In section IV we 
summarize the results and remark on the future direc-
tions.

II. THEORY

A. Quasi-static potential energy surface

In this section we first review the concept of the 
QSPES introduced for the description of molecules in 
strong-fields. The QSPES has been thoroughly dis-
cussed in earlier works \( [13, 36, 38, 54, 60] \), but we here 
give a discussion particularly relevant for the electron 
localization dynamics problem in the dissociation of 
\( \text{H}_2^+ \).

For this problem, the essential physics is contained 
in the two lowest field-free electronic states of the BO 
Hamiltonian, i.e., the \( 1\sigma_g \) and \( 2p\sigma_u \) states, and the full 
molecular wavefunction \( \Psi(\textbf{R}, \textbf{r}, t) \) of the system can be 
expressed as

\[
\Psi(\textbf{R}, \textbf{r}, t) = \chi_g(\textbf{R}, t)\phi_R^g(\textbf{r}) + \chi_u(\textbf{R}, t)\phi_R^u(\textbf{r}).
\]  

(1)

Here \( \chi_g(\textbf{R}, t) \) and \( \chi_u(\textbf{R}, t) \) describe nuclear wavefunc-
tions that exist in the \( 1\sigma_g \) and \( 2p\sigma_u \) states respectively, 
functions of the internuclear distance \( \textbf{R} \) and time \( t \), 
and \( \phi_R^g(\textbf{r}) \) and \( \phi_R^u(\textbf{r}) \) describe the \( 1\sigma_g \) and \( 2p\sigma_u \) 
electronic wavefunction respectively, which parametri-
cally depend on \( \textbf{R} \). Since \( \phi_R^g(\textbf{r}) \) and \( \phi_R^u(\textbf{r}) \) are bond-
ning and anti-bonding combination of 1s atomic orbitals, a coher-
ent superposition of them provides the localized elec-
tronic states \( \phi^\text{left,right}_R(\textbf{r}) = \frac{1}{\sqrt{2}}(\phi^g_R(\textbf{r}) \pm \phi^u_R(\textbf{r})) \) that have 
the electron on either the left or the right proton. These
states form a convenient basis in which to monitor the electron localization asymmetry. In the experiment, interactions of the molecule with the time-delayed infrared laser field in the course of the dissociation provides a coupling of \( \phi^\sigma_R(r) \) and \( \phi^\rho_R(r) \), creating a coherent superposition state, and, instead of Eq. (1), it is instructive to write:

\[
\Psi(R, r, t) = \chi_{\text{left}}(R, t)\phi^\rho_R(r) + \chi_{\text{right}}(R, t)\phi^\rho_R(r) \tag{2}
\]

where \( \chi_{\text{left}}(R, t) \) and \( \chi_{\text{right}}(R, t) \) are defined as the nuclear wavefunctions that exist in connection with left or right along the polarization axis directly relative to the field-free states above are useful to analyse the asymmetry, to understand the time-development of the localization it is helpful to consider a third, time-dependent, basis, the TD quasistatic states, \( \phi^\rho_R(r, t) \), also known as phase-adiabatic states. These states are defined as instantaneous eigenstates of the instantaneous electronic Hamiltonian \( \hat{H}^\text{int}_R(r, t) \), defined by

\[
\hat{H}^\text{int}_R(r, t) = \hat{H}^\text{BO}_R(r) + \hat{v}_\text{laser}(r, t), \tag{3}
\]

i.e.,

\[
\hat{H}^\text{int}_R(r, t)\phi^\rho_R(r, t) = \epsilon^\rho_R(r, t)\phi^\rho_R(r, t) \tag{4}
\]

where \( \epsilon^\rho_R(r, t) \) are the quasistatic potential energy surfaces (QSPESs). Within our two-state model we may write

\[
\phi^\rho_R(r, t) = c^\rho_R(r, t)\phi^\sigma_R(r) + c^\rho_u(r, t)\phi^\rho_R(r), \tag{5}
\]

so that the \( \epsilon^\rho_R(r, t) \) of Eq. (4) are given by the eigenvalue equation:

\[
\begin{bmatrix}
(\phi^\sigma_R | \hat{H}^\text{int}_R | \phi^\sigma_R) \\
(\phi^\sigma_R | \hat{H}^\text{int}_R | \phi^\rho_u) \\
(\phi^\rho_u | \hat{H}^\text{int}_R | \phi^\rho_u) \\
(\phi^\rho_u | \hat{H}^\text{int}_R | \phi^\rho_u)
\end{bmatrix}
\begin{bmatrix}
\epsilon^\rho_R \\
\epsilon^\rho_u
\end{bmatrix} = \epsilon^\rho_R
\begin{bmatrix}
\epsilon^\rho_R \\
\epsilon^\rho_u
\end{bmatrix} \quad (6)
\]

Therefore we can express the QSPESs in terms of the BO states \( \epsilon^\rho_R(R) \) as

\[
\epsilon^\rho(R, t) = \epsilon^\rho(R) \cos^2 \theta(R, t) + \epsilon^\rho(R) \sin^2 \theta(R, t) \quad (7)
\]

and the electronic quasi-static eigenstates in terms of the BO states,

\[
\phi^\rho_R(R, t) = \cos \theta(R, t)\phi^\sigma_R(R) + \sin \theta(R, t)\phi^\rho_u(R) \quad (8)
\]

where the TD mixing parameter \( \theta(R, t) \) is given by

\[
\tan 2\theta(R, t) = \frac{2\langle \phi^\rho_R | \hat{v}_\text{laser} | \phi^\rho_u \rangle}{\epsilon^\rho(R) - \epsilon^\rho(R)}. \tag{9}
\]

The molecular wavefunction expressed in terms of quasi-static states is

\[
\Psi(R, r, t) = \chi^1_QS(R, t)\phi^\rho_R(r, t) + \chi^2_QS(R, t)\phi^\rho_R(r, t) \tag{10}
\]

Note that the nuclear wavefunctions \( \chi^1_QS(R, t) \) and \( \chi^2_QS(R, t) \) that are connected to the quasi-static states \( \phi^\rho_R(r, t) \) and \( \phi^\rho_R(r, t) \) can be expressed in terms of \( \chi_{\text{left}}(R, t) \) and \( \chi_{\text{right}}(R, t) \) as

\[
\chi^1_QS(R, t) = \frac{1}{\sqrt{2}}[\chi_{\text{left}}(R, t)(\cos \theta + \sin \theta) + \chi_{\text{right}}(R, t)(\cos \theta - \sin \theta)] \quad (11)
\]

\[
\chi^2_QS(R, t) = \frac{1}{\sqrt{2}}[\chi_{\text{left}}(R, t)(-\cos \theta + \sin \theta) + \chi_{\text{right}}(R, t)(\cos \theta + \sin \theta)].
\]

which can be used to extract the electron localization from \( \chi^1_QS(R, t) \) and \( \chi^2_QS(R, t) \).

A semi-classical surface-hopping model based on QSPESs has recently been utilized to understand and reproduce the electron localization dynamics and asymmetry in H\(_2^+\). In this approach, an ensemble of classical nuclear trajectories evolve on one QSPES or the other QSPES, making instantaneous hops between them as determined by a Landau-Zener formula. It was shown that the electron localization set in a region where the dynamics is intermediate between adiabatic and diabatic: the ensemble of nuclear trajectories traverses several laser-induced avoided crossings between the QSPESs. This semi-classical method gives asymmetry parameters in reasonably good overall agreement with that obtained from the full TDSE although the details differ. The agreement lends some hope to the use of this semiclassical scheme to simulate coupled electron-ion dynamics in control problems in more complicated systems; however, at the same time a further understanding of the errors in the details is desirable. We will analyze this approach by comparing the QSPESs with the exact TDSE, which we will review in the next section.

**B. Exact time-dependent potential energy surface**

In Ref. [47, 48], it was shown that the full molecular wavefunction \( \Psi(R, r, t) \) which solves the TDSE

\[
\hat{H}\Psi(R, r, t) = i\hbar\partial_t\Psi(R, r, t) \tag{12}
\]

can be exactly factorized to the single product

\[
\Psi(R, r, t) = \chi(R, t)\Phi_R(R, t) \tag{13}
\]

of the nuclear wavefunction \( \chi(R, t) \) and the electronic wavefunction \( \Phi_R(R, t) \) that parametrically depends on
the nuclear positions $\mathbf{R}$ and satisfies the partial
normalization condition
\begin{equation}
\int d\mathbf{r}_e^A |\Phi_{\mathbf{R}, \mathbf{r}}(\mathbf{r}, t)|^2 = 1 \quad \forall \mathbf{R}, t.
\end{equation}

Here, the complete molecular Hamiltonian is
\begin{equation}
\hat{H} = \hat{T}_n(\mathbf{R}) + \hat{V}_n(\mathbf{R}, t) + \hat{H}_{BO}(\mathbf{R}, \mathbf{R}) + \hat{v}_{ext}(\mathbf{r}, t),
\end{equation}
and $\hat{H}_{BO}(\mathbf{R}, \mathbf{R})$ is the BO electronic Hamiltonian,
\begin{equation}
\hat{H}_{BO}(\mathbf{R}, \mathbf{R}) = \hat{T}_e(\mathbf{r}) + \hat{W}_{ee}(\mathbf{r}) + \hat{W}_{en}(\mathbf{r}, \mathbf{R}) + \hat{W}_{nn}(\mathbf{R}).
\end{equation}

Note that $\hat{T}_n = -\sum_{\alpha=1}^{N} \frac{\nabla^2}{2M_{\alpha}}$ and $\hat{T}_e$ is the nuclear and electronic
kinetic energy operators, $\hat{W}_{ee}$, $\hat{W}_{en}$ and $\hat{W}_{nn}$ are the electron-electron, electron-nuclear
and nuclear-nuclear interaction, and $\hat{V}_n(\mathbf{R}, t)$ and $\hat{v}_{ext}(\mathbf{r}, t)$ are time-dependent (TD)
external potentials acting on the nuclei and electrons, respectively.
Throughout this paper $\mathbf{R}$ and $\mathbf{r}$ collectively represent the nuclear and electronic coordinates respectively and $\hbar = 1$.

Returning to Eq. [13], the stationary variations of the quantum mechanical action with respect to $\Phi_{\mathbf{R}, \mathbf{r}}(\mathbf{r}, t)$ and $\chi(\mathbf{R}, t)$ under the condition [14] lead to the following equations of motion for $\chi(\mathbf{R}, t)$ and $\Phi_{\mathbf{R}, \mathbf{r}}(\mathbf{r}, t)$:
\begin{equation}
\left(\hat{H}_{BO}(\mathbf{R}, \mathbf{R}) + \hat{v}_{ext}(\mathbf{r}, t) + \hat{U}_{en}^{\text{coup}}[\Phi_{\mathbf{R}, \mathbf{r}}, \chi] - \epsilon(\mathbf{R}, t)\right) \Phi_{\mathbf{R}, \mathbf{r}}(\mathbf{r}, t) = i\partial_t \Phi_{\mathbf{R}, \mathbf{r}}(\mathbf{r}, t)
\end{equation}
\begin{equation}
= i\partial_t \chi(\mathbf{R}, t).
\end{equation}

Here, $\epsilon(\mathbf{R}, t)$ is the exact nuclear TD PES
\begin{equation}
\epsilon(\mathbf{R}, t) = \left\langle \Phi_{\mathbf{R}, \mathbf{r}}(\mathbf{r}, t) \right| \hat{H}_{BO} + \hat{v}_{ext}(\mathbf{r}, t) + \hat{U}_{en}^{\text{coup}} - i\partial_t \right| \Phi_{\mathbf{R}, \mathbf{r}}(t) \right\rangle_{\mathbf{r}}.
\end{equation}

The symbol $\langle \cdot \rangle_{\mathbf{r}}$ indicates an integration over electronic coordinates only. Note that the PNC makes the factorization [13] unique up to within a $(\mathbf{R}, t)$-dependent
gauge transformation,
\begin{equation}
\chi(\mathbf{R}, t) \rightarrow \tilde{\chi}(\mathbf{R}, t) = e^{-i\theta(\mathbf{R}, t)} \chi(\mathbf{R}, t),
\end{equation}
\begin{equation}
\Phi_{\mathbf{R}, \mathbf{r}}(\mathbf{r}, t) \rightarrow \tilde{\Phi}_{\mathbf{R}, \mathbf{r}}(\mathbf{r}, t) = e^{i\theta(\mathbf{R}, t)} \Phi_{\mathbf{R}, \mathbf{r}}(\mathbf{r}, t),
\end{equation}
and Eqs. [17] and [18] are form invariant under this transformation while the scalar potential and the vector potential transform as
\begin{equation}
\epsilon(\mathbf{R}, t) = \epsilon(\mathbf{R}, t) + \partial_t \theta(\mathbf{R}, t)
\end{equation}
\begin{equation}
\tilde{\mathbf{A}}_{\alpha}(\mathbf{R}, t) = \mathbf{A}_{\alpha}(\mathbf{R}, t) + \nabla_{\alpha} \theta(\mathbf{R}, t)
\end{equation}

The equation for the exact nuclear wavefunction, Eq. [18], is Schrödinger-like, and the TD vector potential [21] and TD scalar potential [19] that appear in it, exactly govern the nuclear dynamics. It is important to note that $\chi(\mathbf{R}, t)$ can be interpreted as the exact nuclear wave-function since it leads to an $N$-body nuclear density, $\Gamma(\mathbf{R}, t) = |\chi(\mathbf{R}, t)|^2$, and an $N$-body current density, $\mathbf{J}_{\alpha}(\mathbf{R}, t) = \frac{1}{\hbar} \text{Im} (\chi^*(\mathbf{R}, t) \nabla_{\alpha} \chi(\mathbf{R}, t)) + \Gamma(\mathbf{R}, t) \mathbf{A}_{\alpha}(\mathbf{R}, t)$, which reproduce the true nuclear $N$-body density and current density [15] obtained from the full wave-function $\psi(\mathbf{r}, \mathbf{R}, t)$.

In our previous work the shape of this exact TD PES has been useful to interpret dynamics for both a strong field process (strong-field dissociation of $\text{H}_2^+$) [47][48] as well as for field-free dynamics of non-adiabatic charge-transfer [49][51]. In particular, in the field-free case, a detailed study of the form of its gauge-dependent and gauge-independent parts proved instructive to understand its effect on the nuclear dynamics, and the structure to be expected for general field-free problems. Importantly, in a mixed quantum-classical description, the gradient of this exact TD PES gives uniquely the correct force on the nuclei, and it was shown, in the field-free case, that an ensemble of classical trajectories evolving on the exact TD PES accurately reproduces the exact nuclear wavepacket dynamics. We now consider a detailed study of the form of the exact TD PES for the present case of dynamics in external fields, with the aims of addressing three questions. First, does running classical nuclear dynamics on the exact TD PES reproduce the dynamics of laser-induced electron localization? Second, how are the QSPESs related to the exact TD PES? Third, can we see hints of the semiclassical surface-hopping method in the exact TD PES?

\section{Results and Discussion}

\subsection{Theoretical Model}

We employ a one-dimensional model of the $\text{H}_2^+$ molecule to study electron localization dynamics
achieved by time-delayed ultra short laser pulses \[7\] \[8\] \[13\]. In the experiment, first a ultraviolet (UV) pulse excites \( H_2^+ \) to the dissociative \( 2p\sigma_u \) state while a second time-delayed infrared (IR) pulse induces electron transfer between the dissociating atoms. In our model, we start the dynamics after the excitation by the UV pulse: the wavepacket starts at \( t = 0 \) on the first excited state (\( 2p\sigma_u \) state) of \( H_2^+ \) as a Frank-Condon projection of the wavefunction of the ground state, and then is exposed to the IR laser pulse. The full Hamiltonian of the system is given by

\[
\hat{H}(R, z, t) = \hat{T}_n(R) + \hat{H}_R^{\text{int}}(z, t) = \hat{T}_n(R) + \hat{W}_{nn}(R) + \hat{W}_{en}(z, R) + \hat{v}_{\text{laser}}(z, t)
\]

(25)

where \( R \) is the internuclear distance and \( z \) is the electronic coordinate as measured from the nuclear center of mass. The kinetic energy terms are \( \hat{T}_n(R) = \frac{1}{2\mu_n} \frac{\partial^2}{\partial R^2} \) and, \( \hat{T}_e(z) = -\frac{1}{2\mu_e} \frac{\partial^2}{\partial z^2} \), respectively, where the reduced mass of the nuclei is given by \( \mu_n = M_{H2}/2 \), and reduced electronic mass is given by \( \mu_e = 2M_H/(2M_H+1) \) (\( M_{H2} \) is the proton mass). The interactions are soft-Coulomb: \( \hat{W}_{nn}(R) = -\frac{1}{\sqrt{1.0+(z-R)^2}} - \frac{1}{\sqrt{1.0+(z+R)^2}} \) (and \( \hat{W}_{ee} = 0 \)). The IR pulse is described within the dipole approximation and length gauge, as \( \hat{v}_{\text{laser}}(z, t) = E(t)\hat{q}_z \), where \( E(t) = E_0 \exp\left[-\left(\frac{t-\Delta t}{\tau}\right)^2\right] \cos(\omega(t-\Delta t)) \), and the reduced charge \( \hat{q}_e = \frac{2M_H}{2M_H+1} \). The wavelength is 800 nm and the peak intensity \( I_0 = E_0^2 = 3.0 \times 10^{12} \text{W/cm}^2 \). The pulse duration is \( \tau = 4.8 \text{fs} \) and \( \Delta t \) is the time delay between the UV and IR pulses. Here we show the results of \( \Delta t = 7 \text{ fs} \).

We propagate the full TDSE

\[
\hat{H}(z, R, t)\Psi(z, R, t) = i\partial_t \Psi(z, R, t)
\]

(26)

umerically exactly to obtain the full molecular wavefunction \( \Psi(z, R, t) \), and from it we calculate the probabilities of directional localization of the electron, \( P_+(-) \), which are defined as \( P_+(-) = \int_{z_>(z<_0)} dz \int dR |\Psi(z, R, t)|^2 \). These are shown as the green solid (\( P_+ \)) and red dashed (\( P_- \)) lines in Fig. 1b. It is evident from this figure that considerable electron localization occurs, with the electron density predominantly localized on the left (negative \( z \)-axis).

Furthermore, we calculate the population dynamics of the BO states \( \phi_R^0(z) \) (green solid) and \( \phi_R^1(z) \) (red dashed) (Fig. 1b) during dissociation, as well as the population dynamics on the 1st quasi-static state \( \phi_{R \text{ QS}}(1)(z, t) \) (green solid) and 2nd quasi-static state \( \phi_{R \text{ QS}}(2)(z, t) \) (red dashed) (Fig. 1c); the relative simplicity of the latter demonstrates the usefulness of the QS basis for laser-induced processes. We then plot the QSPESs \( e^{Q\text{S}(1)}(|R(t)|, t) \) (green solid) and \( e^{Q\text{S}(2)}(|R(t)|, t) \) (red dashed) evaluated at a nuclear trajectory \( |R(t)| \) that tracks the expectation value of the internuclear distance. These results coincide qualitatively with the previous results reported by Kelkensberg et al. \[13\] Panels b, d, and e, suggest that the electron localization is determined by the passage of the dissociating molecule through a regime where the laser-molecule interaction is neither diabatic nor adiabatic. As discussed in the previous section, the semiclassical scheme, with the avoided crossings between the QSPES inducing the trajectories to hop between them, reproduces the general behavior. Next, we will compare the exact TDPS with the QSPES to understand the relation between the two, shed some light on the surface-hopping scheme, and find the exact force on classical nuclei.

![FIG. 1](image-url)

(a) 4.8 fs FWHM 800 nm laser pulse. (b) Electron localization probabilities along the negative (green solid line) and the positive z-axis (red dashed line) as a function of time. (c) Population dynamics during dissociation on the BO state \( \phi_R^0(z) \) (green solid) and \( \phi_R^1(z) \) (red dashed). (d) Population dynamics during dissociation on the 1st quasi-static state \( \phi_{R \text{ QS}}(1)(z, t) \) (green solid) and 2nd quasi-static state \( \phi_{R \text{ QS}}(2)(z, t) \) (red dashed). (e) Quasi-static potential energy surfaces \( e^{Q\text{S}(1)}(R, t) \) (green solid) and \( e^{Q\text{S}(2)}(R, t) \) (red dashed) for a nuclear trajectory \( |R(t)| \) that tracks the expectation value of the internuclear distance. The blue curve shows the transition probability given by a Landau-Zener formula (Eq. 18 of Ref. \[13\]).
B. Exact TDPES vs. QSPES

First we show the exact TDPES for this process in Fig. 2. We calculate the TDPES in the gauge where the vector potential $\mathbf{A}(R, t)$ is zero [49], so the TDPES $\epsilon(R, t)$ is the only potential acting on the nuclear subsystem. It is instructive to express the TDPES as the sum of the gauge-independent term $\epsilon_{gi}(R, t)$ and the gauge-dependent term $\epsilon_{gd}(R, t)$ as done in previous studies [48,49]:

$$\epsilon(R, t) = \epsilon_{gi}(R, t) + \epsilon_{gd}(R, t)$$

(27)

where

$$\epsilon_{gi}(R, t) = \langle \Phi_R(t) | \hat{H}_{BO} + \hat{v}_{laser} + \hat{U}_{coup}^{\text{comp}} | \Phi_R(t) \rangle_z$$

(28)

and

$$\epsilon_{gd}(R, t) = \langle \Phi_R(t) | -i \partial_t | \Phi_R(t) \rangle_z.$$  

(29)

In Fig. 2 $\epsilon(R, t)$ (black solid), $\epsilon_{gi}(R, t)$ (blue solid) and $\epsilon_{gd}(R, t)$ (orange solid) are plotted at nine different times, along with the two lowest BOPESs, $\epsilon_{BO(1)}(R)$ and $\epsilon_{BO(2)}(R)$. (Note that the TDPES $\epsilon(R, t)$ (black solid) and its GD component $\epsilon_{gd}(R, t)$ (orange solid) have been rigidly shifted along the energy axis).

We also plot the exact nuclear density $|\chi(R, t)|^2$ (green solid) and the nuclear density reconstructed from evolving an ensemble of 800 classical trajectories on the exact TDPES (red dashed) at each time. The closeness of these last two curves shows that a mixed quantum-classical scheme for the electron localization process is appropriate and that the exact TDPES $\epsilon(R, t)$ gives the correct force acting on classical nuclei in such a scheme.

In previous work [49-51], step-like features of $\epsilon_{gi}(R, t)$ and $\epsilon_{gd}(R, t)$ in the field-free non-adiabatic process in the vicinity of the avoided crossing have been shown. In particular, after passage through the avoided crossing, where the nuclear wavepacket had spatially separated on two BOPESs, the GI component tracked one BO surface or the other, with a step between them, while the GD component was piecewise flat, but with a step in the same region with opposite sign. The net TDPES was overall more smooth than either of the components. Here, we find again very interesting features of $\epsilon_{gi}(R, t)$ and $\epsilon_{gd}(R, t)$. First note that both $\epsilon_{gi}(R, t)$ and $\epsilon_{gd}(R, t)$ shows many small hills and valleys after the laser-induced nonadiabatic transitions begin, but with opposite slopes to each other, so that these structures largely cancel each other when the exact TDPES $\epsilon(R, t)$ is constructed (much like the near-cancellation of the steps in the field-free case). Like the field-free case, both the GI and GD terms are important to consider to predict the correct nuclear dynamics. Second, in the present strong-field case, unlike the field-free examples studied in [49-51], $\epsilon_{gi}(R, t)$ does not piecewise track one BOPES or the other. However, it does track a density-weighted QSPES, as we will show next.

In Fig. 3, we show $\epsilon(R, t)$ (black solid) (which is again rigidly shifted along the energy axis) and the gauge-invariant part $\epsilon_{gi}(R, t)$ (blue solid) together with the QSPESs $\epsilon_{QS(1)}(R, t)$ (green solid) and $\epsilon_{QS(2)}(R, t)$ (red solid). We find that the oscillations in the gauge-invariant part of exact TDPES $\epsilon_{gi}(R, t)$ (blue solid) tend to step between the two QSPESs: $|\chi_{1}^{\text{QS}}(R, t)|^2$ and $|\chi_{2}^{\text{QS}}(R, t)|^2$ are also plotted in Fig. 3, and we see that $\epsilon_{gi}(R, t)$ tends towards the QSPES whose population is dominant, i.e. when $|\chi_{1}^{\text{QS}}(R, t)|^2$ is larger than $|\chi_{2}^{\text{QS}}(R, t)|^2$ $\epsilon_{gi}(R, t)$ approaches to $\epsilon_{QS(1)}(R, t)$ and when $|\chi_{2}^{\text{QS}}(R, t)|^2$ is larger than $|\chi_{1}^{\text{QS}}(R, t)|^2$ $\epsilon_{gi}(R, t)$ approaches to $\epsilon_{QS(2)}(R, t)$. In fact, $\epsilon_{gi}(R, t)$ lies practically on top of the the weighted average of the quasi-static surfaces $\epsilon_{\text{ave}}^{\text{QS}}(R, t)$:

$$\epsilon_{\text{ave}}^{\text{QS}}(R, t) = \frac{|\chi_{1}^{\text{QS}}(R, t)|^2}{|\chi_{1}^{\text{QS}}(R, t)|^2 + |\chi_{2}^{\text{QS}}(R, t)|^2} \epsilon_{QS(1)}(R, t) + \frac{|\chi_{2}^{\text{QS}}(R, t)|^2}{|\chi_{1}^{\text{QS}}(R, t)|^2 + |\chi_{2}^{\text{QS}}(R, t)|^2} \epsilon_{QS(2)}(R, t)$$

(30)

This is plotted with light blue line in Fig. 3. Therefore the weighted-average of the QSPESs approximates the
gauge-invariant part of exact TDPES $\epsilon_{gi}(R, t)$, but not the full exact TDPES $\epsilon(R, t)$. In fact, this is quite analogous to the previous results on the field-free passage through an avoided crossing [49,51]: there, at the times considered, the density-weighted average collapsed to one BO surface or the other except in the intermediate (step) region, because the spatial separation of the parts of the density projected onto different BO surfaces meant that in the field-free analog to Eq. 30 the prefactors of each term was either one or zero. Here it is evident that the density does not spatially separate (Fig. 3), i.e. the projections on to the QSPESes overlap. One can make entirely analogous statements in both cases: the density-weighted average of the BOPES approximates the gauge-invariant part of exact TDPES $\epsilon_{gi}(R, t)$ in the field-free case, and the density-weighted average of the QSPES approximates the gauge-invariant part of exact TDPES $\epsilon_{gi}(R, t)$ in the presence of strong fields.

To confirm the relationship between $\epsilon_{gi}(R, t)$ and $\epsilon_{ QS}^{av}(R, t)$, we consider the expansion of the complete wavefunction with the two lowest quasi-static states (Eq. [10]). Then the exact electronic conditional wavefunction $\Phi_R (z, t)$ is expressed as:

$$\Phi_R (z, t) = \frac{\xi_1^{QS}(R, t)}{\chi(R, t)} \varphi_R^{(1)} (z, t) + \frac{\xi_2^{QS}(R, t)}{\chi(R, t)} \varphi_R^{(2)} (z, t).$$  

(31)

Then we realize:

$$\langle \Phi_R (z, t) | \hat{H}^{BO} + \hat{v}_{laser} | \Phi_R (z, t) \rangle _z$$

$$= \frac{|\xi_1^{QS}(R, t)|^2}{|\chi(R, t)|^2} \epsilon_{QS}^{(1)} + \frac{|\xi_2^{QS}(R, t)|^2}{|\chi(R, t)|^2} \epsilon_{QS}^{(2)}$$

(32)

Since $\epsilon_{gi}(R, t) = \langle \Phi_R (z, t) | \hat{H}^{BO} + \hat{v}_{laser} | \Phi_R (z, t) \rangle _z + \frac{1}{\overline{\Pi}} \frac{\partial}{\partial \overline{\Pi}} (\Phi_R (z, t) | (-i \frac{\partial}{\partial t} - A(R, t))^2 | \Phi_R (z, t) \rangle _z$, we can conclude

$$\epsilon_{gi}(R, t) \approx \epsilon_{ QS}^{av}(R, t),$$

(33)

because $O(M^{-1})$ term gives a much smaller contribution.

To reproduce the correct dynamics, however the effect of $\epsilon_{gd}(R, t)$ is crucial to include, as in the field-free case studied before [51]. In the gauge we have chosen $A(R, t) = 0$, but we note that if instead we choose the gauge where $\epsilon_{gd}(R, t) = 0$ then the vector potential $A(R, t)$ will be non-zero, and will be responsible for the role of effectively reducing the oscillatory structure in the GI term.

In Fig. 4, we plot the gradient of the different potentials computed on the trajectory of mean nuclear distance $\langle R \rangle (t)$, as a more direct probe of the force on the nuclei. The black line, which is the gradient of the exact TDPES $\frac{\partial}{\partial \overline{\Pi}} \epsilon (\langle R(t) \rangle)$, gives the exact force on the nuclei. First we immediately notice that the gradient of the weighted average of the two QSPES $\frac{\partial}{\partial \overline{\Pi}} \epsilon_{ QS}^{av}(\langle R(t) \rangle)$ (light blue line) (equivalently, the GI component (blue line)) is completely different from the exact force. A semi-classical simulation on the weighted average of the two QSPES would not give the correct nuclear dynamics. We observe instead that, as the localization sets in, the exact force $\frac{\partial}{\partial \overline{\Pi}} \epsilon (\langle R(t) \rangle)$ coincides with the gradient of one or the other QSPES (red or green). This supports the idea of semiclassical surface-hopping between QSPES [13,37,38] at least after the localization begins to set in (time $\sim 6$ fs): the exact force on the nuclei is given by the gradient of the exact TDPES, and, when evaluated at the mean nuclear position, coincides with the force from one QSPES or the other, making transitions between them at their avoided crossings. This explains why the semiclassical simulations of Ref. [13] had a reasonable agreement with the exact results. Furthermore the figure shows the important role of the gauge-dependent part $\epsilon_{gd}(R, t)$; without this term, the force
on the nuclei would be more oscillatory and quite different (blue line in the figure). We note that if instead we choose the gauge where $\epsilon_{gd}(R, t) = 0$ then the vector potential $A(R, t)$ will be responsible for the role of effectively reducing the oscillatory structure in the GI term. As stated above, when we choose the gauge where $\epsilon_{gd}(R, t) = 0$, then the vector potential $A(R, t)$ plays the role of it according to their relationship: $\tilde{A}(R, t) = \int_0^t dt' (-\partial_t \epsilon_{gd}(R, t'))$ [51].

### C. Multiple trajectory Ehrenfest dynamics

Given that there are several avoided crossings during the localization dynamics, one might ask how well a mean-field surface to propagate the electrons would work. To this end, we run a multi-trajectory Ehrenfest calculation [61], and compare the electron and nuclear densities with the exact ones.

In the upper panel of Fig. 5, we plot the conditional electron density $|\Phi_R(z, t)|^2$ obtained from the exact calculation at indicated times. In the lower panel, we plot its squared expansion coefficients of the Born-Oppenheimer expansion $|C_g(R, t)|^2$ (green) and $|C_u(R, t)|^2$ (red) of the exact conditional electronic wave function $\Phi_R(z, t) = \Phi_R^g(z) + C_u(R, t)\Phi_R^u(z)$, along with the nuclear density (black). In Fig. 6 we plotted electron density $|\Phi(z, t)|^2$ obtained from the multiple trajectory Ehrenfest dynamics calculation at the indicated times (plotted for all 800 trajectories $R_{cl}(t)$). The lower panel shows the squared expansion coefficients of the Born-Oppenheimer expansion $|C_g(R_{cl}(t))|^2$ (green) and $|C_u(R_{cl}(t))|^2$ (red) of the electronic wave function $\Phi(z, t|R_{cl}(t))$ obtained from multiple trajectory Ehrenfest dynamics calculation ($\Phi(z, t|R_{cl}(t)) = \Phi_R^g(R_{cl}(t))\Phi_R^g(z) + C_u(R_{cl}(t))\Phi_R^u(z)$).

We also show the nuclear densities reconstructed from the distribution of classical trajectories obtained from multiple trajectory Ehrenfest dynamics calculation (black circle line).

Comparing the top panels of these figures shows that Ehrenfest dynamics gets the overall structure of the electronic conditional probability reasonably well, however not exactly; in fact, these differences lead to an incorrect prediction of the localization asymmetry. For example, at $t = 12.0$ fs at the internuclear separation where the nuclear density is peaked, the projections shown in the lower panels, onto the BO surfaces predicted by Ehrenfest are each close to 0.5, while the exact are closer to 0.6 and 0.4. Given the nature of the BO $g$ and $u$ states in terms of the left and right basis (Sec. [IA]), this suggests the localization asymmetry predicted by Ehrenfest is close to 1:0 while the exact is close to 0.8:0.2. Indeed this is verified by the calculation of the asymmetry. Further, throughout the width of the nuclear wavepacket, the Ehrenfest projections remain close to 0.5, while the exact projections fall away, indicating there is a larger degree of decoherence in the exact dynamics, missed in the Ehrenfest dynamics. The differences in the conditional wavefunction and the BO projections is even greater where the nuclear density is small ($R = 8 \sim 10$ and $R = 12 \sim 14$).

In the field-free problem of non-adiabatic charge-transfer [49,51,62], multiple-trajectory Ehrenfest dynamics failed, and this might have been expected given that the density spatially separates (branches) onto two
different BO surfaces. In the present case, the nuclear density does not split in space, and actually predicts the nuclear dynamics quite well, but the errors in the electronic dynamics are more significant. Further, it is the same potential that evolves the electrons in the Ehrenfest dynamics scheme, we have to go beyond the traditional methods such as surface-hopping or Ehrenfest methods. Our results here encourage the development of mixed quantum-classical schemes based on Eqs (17) and (18) to simulate strong-field processes.

**Acknowledgments:** Partial support from the Deutsche Forschungsgemeinschaft (SFB 762), the European Commission (FP7-NMP-CRONOS), and the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences and Biosciences under award DE-SC0008623 (NTM), is gratefully acknowledged.

**REFERENCES**

[1] F. Krausz and M. Ivanov, Rev. Mod. Phys. 81, 163 (2009).
[2] M. J. J. Vrakking, Phys. Chem. Chem. Phys. 16, 2775 (2014).
[3] F. Lépine, M. Y. Ivanov, and M. J. J. Vrakking, Nature Photon. 8, 195 (2014).
[4] S. Haessler et al., Nature Phys. 6, 200 (2010).
[5] P. B. Corkum and F. Krausz, Nature Phys. 3, 381 (2007).
[6] E. Calegari et al., Science 346, 336 (2014).
[7] G. Sansone et al., Nature 465, 763 (2010).
[8] F. He, C. Ruiz, and A. Becker, Phys. Rev. Lett. 99, 083002 (2007).
[9] D. Ray et al., Phys. Rev. Lett. 103, 223201 (2009).
[10] K. P. Singh et al., Phys. Rev. Lett. 104, 023001 (2010).
[11] B. Fischer et al., Phys. Rev. Lett. 105, 223001 (2010).
[12] C. R. Calvert et al., J. Phys. B: At. Mol. Opt. Phys. 43, 011001 (2010).
[13] F. Kelkensberg, G. Sansone, M. Y. Ivanov, and M. Vrakking, Phys. Chem. Chem. Phys. 13, 8647 (2011).
A set of 800 trajectories is propagated according to

\[ \mu_n \frac{d}{dt} v_{cl}(t) = - \int d\mathbf{r} \Phi(\mathbf{r}, t | R_{cl}(t)) \left( \frac{d}{d\mathbf{R}} H_\text{int}^{\text{cl}}(\mathbf{r}, t) \right) \Phi(\mathbf{r}, t | R_{cl}(t)) \]  

(34)

and

\[ i \frac{\partial}{\partial t} \Phi(\mathbf{r}, t | R_{cl}(t)) = H_\text{int}^{\text{cl}}(\mathbf{r}, t) \Phi(\mathbf{r}, t | R_{cl}(t)), \]  

(35)

where the initial conditions are sampled from the phase-space distribution corresponding to \( \chi(\mathbf{R}, t = 0) \).