Universal Steps Guiding the Branching of the Nuclear Probability Density over Nonadiabatic Electronic Transitions

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In the conditional approach to molecular dynamics the electron-nuclear wavefunction is exactly decomposed into an ensemble of nuclear wavepackets governed by conditional time-dependent potential-energy surfaces (C-TDPEs) [G. Albareda, et al., Phys. Rev. Lett. 105, 123002 (2014)]. Employing a one-dimensional model system we show that for strong nonadiabatic couplings the C-TDPEs exhibit steps that bridge between piecewise adiabatic shapes. A detailed analysis of the steps sheds light into the ultimate nature of electron-nuclear correlations and its comparison with the discontinuities that emerge in the exact factorization of the molecular wavefunction brings us to claim their universality in theories without Born-Oppenheimer potential-energy surfaces.

The description of correlated electron-nuclear dynamics remains a formidable challenge in condensed-matter physics and theoretical chemistry [1–6]. Relying on the Born-Huang expansion of the full molecular wavefunction, a majority of approaches that provide a numerically accurate description of the so-called “nonadiabatic” processes require the propagation of a set of many-body nuclear wavepackets on a coupled set of Born-Oppenheimer potential-energy surfaces (BOPEs) [7–13]. Whenever electron-nuclear coherence effects are unimportant, efficient mixed quantum-classical propagation techniques can be used [14–20]. However, in order to account for strong correlations, the access to quantum features of the nuclear motion such as spreading, tunnelling or splitting is crucial. Hence, a reliable description of molecular dynamics becomes very expensive due to the calculation of the full BOPEs, a (time-independent) problem that scales exponentially with both the nuclear and electronic degrees of freedom [21–23]. Towards a more efficient description of correlated electron-nuclear dynamics, avoiding the computational costs of calculating the BOPEs and non-adiabatic couplings, two alternative formally exact frameworks, viz. the exact factorization (EF) [24] and the conditional decomposition (CD) [25], have been recently proposed.

The CD approach to molecular dynamics allows for the decomposition of the electron-nuclear wavefunction into an ensemble of nuclear wavefunctions effectively governed by conditional time-dependent potential-energy surfaces (C-TDPEs) [25]. While keeping the theory at the full configuration level, this approach allows for the use of trajectory-based statistical techniques to circumvent the calculation of the BOPEs and nonadiabatic couplings. Furthermore, this approach avoids artifacts coming from the tracing out of the electronic degrees of freedom and, hence, it allows to draw clear connections between different formally exact frameworks. In this Letter we investigate the generic features of the exact C-TDPEs in the presence of strong nonadiabatic couplings. A major result will be that the exact C-TDPEs exhibit discontinuous steps connecting different BOPEs analogous to paradigmatic features of the effective time-dependent potential that governs the nuclear dynamics in the EF framework. By establishing a formal connection between the CD and the EF frameworks we will discuss the universality of these features in theories without BOPEs.

Throughout this Letter we use atomic units, and electronic and nuclear coordinates are collectively denoted by $\mathbf{r} = \{r_1, \ldots, r_N\}$ and $\mathbf{R} = \{R_1, \ldots, R_N\}$, where $N_e$ and $N_n$ are the total number of electrons and nuclei. We have recently proved [25] that the full (non-relativistic) electron-nuclear wavefunction $\Psi(\mathbf{r}, \mathbf{R}, t)$ can be exactly decomposed into an ensemble of conditional nuclear wavefunctions, $\psi_\alpha(\mathbf{R}, t) := \int \delta(r_\alpha(t) - \mathbf{r}) \Psi(\mathbf{r}, \mathbf{R}, t) d\mathbf{r}$, provided that the electronic trajectories $\{r_\alpha(t) \equiv r_{1,\alpha}(t), \ldots, r_{N_e,\alpha}(t)\}$ probe the electronic support of $|\Psi(\mathbf{r}, \mathbf{R}, t)|^2$ at any time $t$ [25]. These conditional wavefunctions can be used to reconstruct the full wavefunction (or equivalently any observable) through $\Psi(\mathbf{r}, \mathbf{R}, t) = \mathcal{D}_\mathbf{R}[\psi_\alpha]$, where $\mathcal{D}_\mathbf{R}[f(a_\alpha)] \equiv \sum_a = 1 \delta(a_\alpha - a)f(a_\alpha)/\sum_a = 1 \delta(a_\alpha - a)$ when $\sum_a = 1 \delta(a_\alpha - a) \neq 0$ and it is zero otherwise. Throughout this work we will use quantum trajectories defined through $r_{\xi,\alpha}(t) = r_{\xi,\alpha}(t_0) + \int_{t_0}^t \dot{r}_{\xi,\alpha}(t') dt'$ and $R_{\nu,\alpha}(t) = R_{\nu,\alpha}(t_0) + \int_{t_0}^t \dot{R}_{\nu,\alpha}(t') dt'$, where electronic
and nuclear velocities are given by \( \dot{r}_{\xi,\alpha} = \nabla_{\xi} S |_{r_{\alpha}, \mathbf{r}_{\alpha}} \) and \( R_{\alpha,\alpha} = (\nabla_{\xi} S / M_{\xi}) |_{r_{\alpha}, \mathbf{r}_{\alpha}} \), and \( S \) is the phase of the full electron-nuclear wavefunction \( \Psi = |\Psi| e^{iS} \) [27] [28]. For the sake of simplicity, we will omit from now on the explicit dependence of the trajectories on time, i.e. \( \{ r_{\alpha} \} \equiv \{ r_{\alpha}(t) \} \). In the absence of time-dependent external fields, the molecular system is described by the Hamiltonian \( \hat{H} = \hat{T}_{n}(\mathbf{r}) + \hat{T}_{\alpha}(\mathbf{r}) + W(\mathbf{r}, \mathbf{R}, t) \), where \( \hat{T}_{n} = -\sum_{\alpha=1}^{N_{n}} \frac{\nabla_{\xi}^{2}}{2|\Psi|^{2}|_{r_{\alpha}}} \) and \( \hat{T}_{\alpha} = -\sum_{\alpha=1}^{N_{\alpha}} \nabla_{\xi}^{2}/2M_{\xi} \) are the electronic and nuclear kinetic energy operators, and \( W(\mathbf{r}, \mathbf{R}, t) = W_{\text{ee}}(\mathbf{r}) + W_{\text{nn}}(\mathbf{R}) + W_{\text{en}}(\mathbf{r}, \mathbf{R}) \) denotes the internal Coulombic interactions. The wavefunctions \( \psi_{\alpha}(\mathbf{R}, t) \) obey the following equations of motion [29]:

\[
\dot{i}d_{\xi}\psi_{\alpha}(\mathbf{R}, t) = \left\{ \hat{T}_{n}(\mathbf{R}) + V_{\alpha}(\mathbf{R}, t) \right\} \psi_{\alpha}(\mathbf{R}, t),
\]

where the effective potentials \( V_{\alpha}(\mathbf{R}, t) = W_{\alpha}(\mathbf{R}, t) + K_{\alpha}(\mathbf{R}, t) + A_{\alpha}(\mathbf{R}, t) \) are named timedependent potential energy surfaces (C-TDPESS). Each C-TDPESS consists of three terms: the conditional Coulombic potential \( W_{\alpha}(\mathbf{R}, t) = W(\mathbf{r}_{\alpha}, \mathbf{R}, t) \), the kinetic correlation potential, \( K_{\alpha}(\mathbf{R}, t) = \frac{\dot{\hat{r}}_{\xi} |_{r_{\alpha}}}{r_{\alpha}} \), and an advective potential, \( A_{\alpha}(\mathbf{R}, t) = i \sum_{\xi=1}^{N_{\xi}} \frac{\nabla_{\xi}\psi_{\alpha}}{2|\Psi|^{2}|_{r_{\alpha}}} \cdot \dot{\hat{r}}_{\xi,\alpha} \). As shown in Eq. (1), each nuclear wavefunction \( \psi_{\alpha}(\mathbf{R}, t) \) represents a 3\( N_{\alpha} \)-dimensional slice of the full molecular wavefunction (taken along the nuclear coordinates) whose evolution is, in general, non-unitary due to the complex nature of the kinetic and advective potentials.

Note that the propagation of the nuclear equations of motion in Eq. (1) does not require the calculation of the BOPES. This makes the method particularly advantageous when studying processes that involve many BOPESs, as in laser-induced dynamics or scattering from metallic surfaces. Since the initial conditions of a trajectory-based simulation can be generated with importance-sampling techniques, conditional decompositions can be exploited to circumvent the problem of storing and propagating a many-particle wave function whose size scales exponentially with the number of particles. In this respect, we emphasize that the conditional decomposition of the molecular wave function in Eq. (1) is only one among many other possible conditional decompositions [25] [29] [32].

To analyze the C-TDPESSs, we decompose \( V_{\alpha} \) into real and imaginary parts \( V_{\alpha}^{R} = W_{\alpha}(\mathbf{R}, t) + K_{\alpha}^{R} + A_{\alpha}^{R} \) and \( V_{\alpha}^{I} = K_{\alpha}^{I} + A_{\alpha}^{I} \), where

\[
K_{\alpha}^{R} = \sum_{\xi=1}^{N_{\xi}} Q_{\xi,\alpha}^{\epsilon} + \frac{(\nabla_{\xi} S)^{2}}{2 |_{r_{\alpha}}} ; \quad K_{\alpha}^{I} = -\sum_{\xi=1}^{N_{\xi}} \frac{\nabla_{\xi} |_{r_{\alpha}}}{2 |\Psi|^{2}|_{r_{\alpha}}} ; \quad A_{\alpha}^{R} = \sum_{\xi=1}^{N_{\xi}} \frac{\nabla_{\xi} |_{r_{\alpha}}}{2 |\Psi|^{2}|_{r_{\alpha}}} \cdot \dot{\hat{r}}_{\xi,\alpha},
\]

and

\[
A_{\alpha}^{I} = \sum_{\xi=1}^{N_{\xi}} \nabla_{\xi} S |_{r_{\alpha}} \cdot \dot{\hat{r}}_{\xi,\alpha} ; \quad A_{\alpha}^{I} = \sum_{\xi=1}^{N_{\xi}} \frac{\nabla_{\xi} |_{r_{\alpha}}}{2 |\Psi|^{2}|_{r_{\alpha}}} \cdot \dot{\hat{r}}_{\xi,\alpha},
\]

are respectively the real and imaginary parts of the kinetic and advective correlation potentials. In Eq. (3) we have respectively defined the \( \xi \)-th components of the so-called electronic quantum potential [27] [28] and the current probability density as \( Q_{\xi,\alpha}^{\epsilon} = \frac{1}{2} \nabla_{\xi}^{2} |\Psi|^{2}|_{r_{\alpha}} \) and \( J_{\xi} = |\Psi|^{2} \nabla_{\xi} S \). While the classical kinetic potential, \( Q_{\xi,\alpha}^{K} \), is in general a smooth function of the nuclear coordinates, we expect the quantum contributions, \( Q_{\xi,\alpha}^{Q} \), and \( K_{\alpha}^{I} \), to be rather “discontinuous” because of their dependence on the inverse of the conditional nuclear probability density. Notice that these last two quantities are implicit functions of the electronic coordinates. Specifically, the electronic quantum potential \( Q_{\xi,\alpha}^{Q} \) accounts for changes of the curvature of the full probability density along the electronic coordinates (as a function of the nuclear positions). Alternatively, \( K_{\alpha}^{I} \) describes the dispersion (e.g. spreading or splitting) of the full wavefunction in the electronic direction. Both contributions become large in the vicinity of a node, and thus, they will be important whenever the full probability density splits apart along the electronic coordinates. The advective correlations in Eq. (3) are weighted by electronic velocities, \( \dot{\hat{r}}_{\xi,\alpha} \), and hence, they will be significant only during a fast reconfiguration of the electronic degrees of freedom.

To study the features of the exact C-TDPESSs during nonadiabatic processes in the CD approach, we employ the model introduced by Shin and Metiu [33], which consists of three ions and a single electron. Two ions are fixed at a distance \( L = 19.0a_{0} \), and the third ion and the electron are free to move in one dimension along the line joining the fixed ions. The Hamiltonian for this system reads:

\[
\hat{H}(r, R) = -\frac{1}{2} \frac{\partial^{2}}{\partial r^{2}} - \frac{1}{2M} \frac{\partial^{2}}{\partial R^{2}} + \frac{1}{|\frac{1}{2} - R|} + \frac{1}{|\frac{1}{2} + R|}
\]
where the symbols \( r \) and \( R \) are replaced by \( r \) and \( R \), and the coordinates of the electron and the movable nucleus are measured from the center of the two fixed ions. We choose the remaining parameters to be the same as in reference \(^{33}\), i.e. \( M = 1836a.u. \) and \( R_i = 5.0a_0, R_f = 4.0a_0, \) and \( R_e = 3.1a_0 \) such that the first BOPES, \( \epsilon_{BO}^{(1)}(r) \), is strongly coupled to the second, \( \epsilon_{BO}^{(2)} \) around \( R_{ac} = -2a_0 \). The coupling to the rest of the BOPESs is negligible. Note that the time-independent electronic problem is fully characterized through the so-called electronic Hamiltonian, i.e. \( (\hat{T}_e + W)\Phi_R^{(i)}(r) = \epsilon_{BO}^{(i)}(R)\Phi_R^{(i)}(r) \). We suppose the system to be initially excited to \( \epsilon_{BO}^{(2)} \) and the initial nuclear wavefunction to be a Gaussian wavepacket with \( \sigma = 1/\sqrt{2.65} \), centered at \( R = -4.0a_0 \), i.e. the initial full wavefunction is \( \Psi(r, R, t_0) = Ae^{-(R-R_0)^2/\sigma^2}\epsilon_{BO}^{(1)}(r) \) with \( A \) being a normalization constant. On the left panel of Fig. 1 we show the first three BOPESs together with the evolution of the adiabatic populations (in the inset). The right panel of Fig. 1 shows the first two Born-Oppenheimer states \( \Phi^{(1)}_R(r) \) and \( \Phi^{(2)}_R(r) \) along with the evolution of three selected trajectories \{\( r_\alpha, R_\alpha \)\} labeled \( \alpha = 1,2,3 \). Analyzed below, in Fig. 2 we present four time snapshots containing relevant information about the C-TDPESs as well as the conditional nuclear wavefunctions. For the sake of clarity we also define approximated real and imaginary components of the C-TDPESs respectively as \( V_{\alpha,app}^R = Q_{\alpha}^e + W_\alpha \) and \( V_{\alpha,app}^I = K_\alpha \).

At the initial time \( (t_0 = 0fs) \), due to the choice of \( \Psi(r, R, r_0) \), the C-TDPESs are real, \( \alpha \)-independent, and by construction all equal to the first excited BOPES \( \epsilon_{BO}^{(2)} \):

\[
\begin{align*}
V_\alpha = \frac{\hat{T}_e \Phi^{(2)}_R(r)}{\Phi^{(2)}_R(r)}_{r_\alpha} + W_\alpha = V_{\alpha,app}^R = \epsilon_{BO}^{(2)}, \quad \forall \alpha
\end{align*}
\]

where we used that \( Q_{\alpha}^e(R, t_0) = \hat{T}_e \Phi^{(2)}_R(r)/\Phi^{(2)}_R(r) \) when \( \partial_t S = 0 \) (a more detailed analysis of the C-TDPESs in terms of the Born-Huang expansion of the molecular wavefunction can be found in SM A). Since \( \Psi(r, R, r_0) \) is not an eigenstate of the Hamiltonian in \( \{4\} \), it evolves in time. As it is made clear in the right panels of Fig. 1 at \( t = 13.44fs \), the trajectories (\( r_2, R_2 \)) and (\( r_3, R_3 \)), associated respectively with the conditional wavefunctions \( \psi_2 \) and \( \psi_3 \), are running straight (i.e. \( r_{2,3} \approx 0 \)) from the support of \( \Phi^{(2)}(r) \) to fall in the support of \( \Phi^{(1)}(r) \). For \( \alpha = 2,3 \) the C-TDPESs are real \((V_{2,3}^I = 0)\) and satisfy \( V_{2,3} \approx V_{2,3,app}^R \) with \( Q_{2,3}^e(R < R_{ac}) \approx \hat{T}_e \Phi^{(2)}_R(r)/\Phi^{(2)}_R(r) \) and \( Q_{2,3}^e(R > R_{ac}) \approx \hat{T}_e \Phi^{(1)}_R(r)/\Phi^{(1)}_R(r) \). Therefore, as can be seen from Fig. 2 (bottom left panel), the C-TDPESs resemble diabatic potential-energy surfaces, coinciding with \( \epsilon_{BO}^{(2)} \) for \( R < R_{ac} \) and smoothly going through the avoided crossing region to follow \( \epsilon_{BO}^{(1)} \) for \( R > R_{ac} \). Conversely, trajectory \( (r_1, R_1) \) tunnels from one Coulomb potential well \( W_\alpha \) to the other, staying most of the time in the support of \( \Phi^{(2)}_R(r) \). The velocity \( \dot{r}_1 \) is now large due to the fast reconfiguration of the electronic degrees of freedom, and hence \( V_1 \) shows important adveective contributions. Notice also that both \( V^R_4 \) and \( V^I_4 \) show steep peaks that originate in the full configuration space as the full probability density starts to split up along the electronic coordinates (left panels b) and c) of Fig. 2). At the later time \( t = 19.32fs \), the adveective correlation and classical kinetic terms become once more negligible, and therefore \( V_5 \approx V_{\alpha,app}^R + V_{\alpha,app}^I \). While \( (r_1, R_1) \) stays preferentially in the support of \( \Phi^{(2)}_R(r) \), the trajectories \( (r_2, R_2) \) and \( (r_3, R_3) \) are mainly sampling the support of \( \Phi^{(1)}_R(r) \) (see the right panel of Fig. 1). The conditional wavefunctions \( \psi_1, \psi_2 \) and \( \psi_3 \) are now linear combinations of \( \Phi^{(2)}_R(r) \) or \( \Phi^{(1)}_R(r) \) (possibly showing contributions from higher energetic Born-Oppenheimer states) \( ^{33} \). This mixture leads to the formation of the step observed for \( V_1 \) around \( R = 1.5a_0 \), and also to wiggles accompanying in the C-TDPESs \( V_2 \) and \( V_3 \). All these features indicate the nonadiabatic nature of the conditional wavefunctions and can be directly associated with the formation of nodes in the full probability density. Concretely, as shown in panels b) and c) of Fig. 2 the splitting of the full probability density can be understood as the result of the formation of dynamical nodes (originating from kinetic correlations) that move across the full configuration space as if they were knife edges. Finally, at time \( t = 31.5fs \), the full molecular wavefunction has been split both along the electronic and nuclear directions. While the three conditional wavefunctions, \( \psi_1, \psi_2 \) and \( \psi_3 \), still embody contributions from both \( \Phi^{(2)}_R(r) \) and \( \Phi^{(1)}_R(r) \), these contributions are now very well separated along the nuclear coordinates with a minimum at around \( R_{sp} = 4a_0 \) (see also Fig. 1 right panel). For nuclear coordinates less than \( R_{sp} \), the support of the full probability density perfectly fits in the support of the first excited Born-Oppenheimer state \( \Phi^{(2)}_R \), while for \( R > R_{sp} \) it mainly falls in the ground state \( \Phi^{(1)}_R \). As a direct consequence, the quantum electronic potential acquires a discontinuity, i.e. \( Q_{\alpha}^e(R < R_{sp}) \approx \hat{T}_e \Phi^{(2)}_R(r)/\Phi^{(2)}_R(r) \) while \( Q_{\alpha}^e(R > R_{sp}) \approx \hat{T}_e \Phi^{(1)}_R(r)/\Phi^{(1)}_R(r) \). The real parts of the C-TDPESs are therefore piecewise connecting adiabatic surfaces, i.e. \( V^R_\alpha \approx V^R_{\alpha,app} \approx \epsilon_{BO}^{(1)} \) for \( R > R_{sp} \), and \( V^I_\alpha \approx V^I_{\alpha,app} \approx \epsilon_{BO}^{(2)} \) for \( R < R_{sp} \) (the reader is again referred to SM A for further discussion). In the transition between these two regions (at around \( R_{sp} \)), the conditional wave functions \( \psi_1, \psi_2 \) and \( \psi_3 \) become linear combinations of (at least) the lowest two adiabatic electronic states. As a result, the C-TDPESs exhibit abrupt peaks, both real and imaginary, mainly originating from the potentials \( Q^e_\alpha \) and \( K^R_\alpha \). In the full configuration space (left panels in
wavefunctions, \( \psi \). In the background (in copper color scale), full configuration dependence of a) the electron-nuclear potential energy \( W(r,R) \), and b) and c) respectively the real and imaginary components of the kinetic correlation potential \( K^{\alpha}(r,R) \). RIGHT PANELS: In 1), 2) and 3) (bottom) we display the conditional probability densities with the first three BOPESs (dotted red = \( \epsilon \), blue = \( \epsilon_{BO} \), and green = \( \epsilon_{BO} \) lines) and the real part of the C-TDPESs \( V^{\alpha\omega} = W^{\alpha} + K^{\alpha} + A^{\alpha} \) (in magenta). For comparison we also show the potential \( V^{\alpha\omega}_{\alpha,app} = Q^{\alpha} + W^{\alpha} \) (green circles). In 1), 2) and 3) (middle): Electronic quantum potential alone \( Q^{\alpha} \). In 1), 2) and 3) (top): Imaginary part of the C-TDPESs \( V^{\alpha\omega}_{\alpha,app} = K^{\alpha} + A^{\alpha} \) (magenta line) along with the approximated potential \( V^{\alpha\omega}_{\alpha,app} = K^{\alpha} \) alone (green circles).

Fig. 2. LEFT PANELS: Contour lines of the full electron-nuclear probability density (in white) together with three conditional wavefunctions, \( \psi_1(R,t) \), \( \psi_2(R,t) \), and \( \psi_3(R,t) \) (dotted black lines), defined along with the trajectories \( \{ r_{\alpha=1,2,3}, R_{\alpha=1,2,3} \} \) (in cyan). In the background (in copper color scale), full configuration dependence of a) the electron-nuclear potential energy \( W(r,R) \), and b) and c) respectively the real and imaginary components of the kinetic correlation potential \( K^{\alpha}(r,R) \). RIGHT PANELS: In 1), 2) and 3) (bottom) we display the conditional probability densities with the first three BOPESs (dotted red = \( \epsilon \), blue = \( \epsilon_{BO} \), and green = \( \epsilon_{BO} \) lines) and the real part of the C-TDPESs \( V^{\alpha\omega} = W^{\alpha} + K^{\alpha} + A^{\alpha} \) (in magenta). For comparison we also show the potential \( V^{\alpha\omega}_{\alpha,app} = Q^{\alpha} + W^{\alpha} \) (green circles). In 1), 2) and 3) (middle): Electronic quantum potential alone \( Q^{\alpha} \). In 1), 2) and 3) (top): Imaginary part of the C-TDPESs \( V^{\alpha\omega}_{\alpha,app} = K^{\alpha} + A^{\alpha} \) (magenta line) along with the approximated potential \( V^{\alpha\omega}_{\alpha,app} = K^{\alpha} \) alone (green circles).

Fig. 2, these features are now directly translated into deep wells/barriers that keep the full probability density well separated into three pieces.

Recently, the concept of the TDPES has been used to shed light into the origins of the branching of the nuclear probability density in nonadiabatic transitions. In [34], Abedi et al. report properties of the TDPES that closely match the merits that we have just described for the ensemble of C-TDPESs: far from the region of avoided crossings (when the nonadiabatic couplings are negligible) the TDPES coincide with the adiabatic BOPESs, while in their neighborhood exhibits nearly discontinuous steps that connect two different adiabatic BOPESs. The same behavior was also observed for the C-TDPESs derived in this work and therefore it is worth investigating if these discontinuities have a common, universal origin. To this end, by virtue of the EF theorem, we rewrite the conditional nuclear wavefunction as a direct product of conditional electronic and nuclear wavefunctions, i.e., \( \psi_\alpha(R,t) = \Phi_R(r_\alpha,t)\chi(R,t) \). By inserting this Ansatz into Eq. (1), equations of motion for both electronic and nuclear factors can be derived. Here, the nuclear wavefunction, \( \chi(R,t) \), plays a central role in establishing a relation between the EF and CD frameworks. For the model system studied here [36], the equation of motion for \( \chi(R,t) \) simply reads

\[
i\partial_t \chi(R,t) = \left\{ \hat{T}_n(R) + \epsilon(R,t) \right\} \chi(R,t),
\]

where the exact TDPES, \( \epsilon(R,t) \), effectively governs the nuclear dynamics and can be written in terms of the C-TDPESs as:

\[
\epsilon(R,t) = \frac{\int \mathcal{D}_r |\psi_\alpha|^2 V_{\alpha}\,dr}{\int \mathcal{D}_r |\psi_\alpha|^2\,dr} + O(M_n^{-1}) + \epsilon_{gd}(R,t).
\]

The third term on the r.h.s of Eq. (6), \( \epsilon_{gd}(R,t) \), depends on the specific choice of the gauge, while the second term, \( O(M_n^{-1}) \), is most of the time negligible because it depends on the inverse of the nuclear mass (see SM B). We are left with the first term on the r.h.s of Eq. (6), which establishes a direct connection between the TDPES concept, i.e., a single function of the nuclear coordinates and time, and the C-TDPESs, which are, one-by-one, functions of the nuclear coordinates and time that depend parametrically on the electronic degrees of freedom through the trajectories \( \{ r_\alpha \} \). As stated in Eq. (6), in the TDPES of the EF approach, discontinuities can be understood to emerge through an ensemble average of C-
TDPESSs, $V_\alpha$, which are integrated along the conditional probability densities $|\psi_\alpha|^2$ and weighted afterwards by the nuclear probability density, $\int \hat{D}_r [|\psi_\alpha|^2]dr = \int |\Psi|^2dr$.

Hence, the main difference between the BOPESSs and the effective time-dependent potentials that arise in the EF and CD frameworks, is that the first are defined independently from the nature and the position of the total electron-nuclear wavefunction, while in the time-dependent case, the effective potentials have a direct dependence on the full wavefunction (either through the first term in the r.h.s of Eq. [6] in the EF framework or through the quantum potential in Eq. [2] in the CD framework), which can induce discontinuities. Within the Born-Oppenheimer picture, the nuclear wavepacket can populate different BOPESSs and reproduce in this way coherent wavepacket branching during a nonadiabatic process. In the EF or in the CD discussed here the same physics seems to be universally described by abrupt steps in the effective time-dependent potentials that drive the nuclear wavepacket dynamics. These steps connect different portions of the underlying BOPESSs, splitting the support of the nuclear wavepacket into subsets that are associated, piecewise, to different portions of the corresponding BOPESSs.

To summarize, we have reported discontinuities in the exact C-TDPESSs for the specific situation where, according to the standard Born-Oppenheimer picture, the nuclear wavepacket splits at the avoided crossing of two BOPESSs. The C-TDPESSs are the only potentials that govern the dynamics of the conditional nuclear wavefunctions and, therefore, provide us with an alternative way of visualizing and interpreting nonadiabatic processes without the need of BOPESSs or nonadiabatic couplings. Our study reveals that the shape and position of discontinuous steps connecting different BOPESSs is mainly dictated by the electronic quantum potential, $Q^e_\alpha$, which can be understood as a clear-cut signature of the ultimate quantum nature of electron-nuclear correlations. In our analysis we have also identified a very close correspondence between the C-TDPESSs and the effective potentials that arises in the EF approach, both showing the same kind of steps during the branching of the nuclear probability density. A formal connection between the CD and the EF frameworks brought us to discuss on the universality of these discontinuities in molecular dynamics theories without BOPESSs. In this respect, it is worth mentioning that other attempts to reduce the complexity of the time-dependent Schrödinger equation, such as in time-dependent density-functional theory, also lead to the emergence of striking discontinuities in the effective time-dependent potentials that govern the reduced variables of interest. This is the case, e.g., in the field of electron-electron correlated dynamics, where the nature of such discontinuities is currently under study \[37\][39].

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[26] The electronic support of the full probability density \( |\Psi(r, R, t)|^2 \) can be defined as: supp\((|\Psi(r, R, t)|^2) = \{ r \in r \mid |\Psi(r, R, t)|^2 > \lambda \} \), where \( \lambda \) denotes a given lower bound of the probability density.


[35] As shown in SM A, the conditional wavefunctions can be always written as a linear combination of Born-Oppenheimer states, i.e. \( \psi_\alpha(r, t) = \sum_j C_j(R, t) \Phi_j^{(\alpha)}(r) \).

[36] In the EF approach the coupling between the nuclear and the electronic degrees of freedom is exactly mediated by the TDPES and time-dependent Berry connection up to a gauge transformation. For one-dimensional problems, i.e. if there is only one nuclear degree of freedom, the gauge can be fixed such that the Berry phase is always zero [7].