Dynamical Steps that Bridge Piecewise Adiabatic Shapes in the Exact Time-Dependent Potential Energy Surface

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We study the exact time-dependent potential energy surface (TDPES) in the presence of strong nonadiabatic coupling between the electronic and nuclear motion. The concept of the TDPES emerges from the exact factorization of the full electron-nuclear wave function [A. Abedi, N. T. Maitra, and E. K. U. Gross, Phys. Rev. Lett. **105**, 123002 (2010)]. Employing a one-dimensional model system, we show that the TDPES exhibits a dynamical step that bridges between piecewise adiabatic shapes. We analytically investigate the position of the steps and the nature of the switching between the adiabatic pieces of the TDPES.

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The description of coupled electron-nuclear motion is one of the biggest challenges in condensed-matter physics and theoretical chemistry. Fundamental to our understanding is the adiabatic separation of electronic and nuclear motion embodied in the Born-Oppenheimer (BO) approximation. It allows one to visualize—approximately—a molecule as a set of nuclei moving on a single potential energy surface generated by the electrons in a specific electronic eigenstate. The BO approximation breaks down when two or more Born-Oppenheimer potential energy surface (BOPES) come close or cross. Some of the most fascinating and most challenging molecular processes occur in the regime where the BO approximation is not valid, e.g., ultrafast nuclear motion through conical intersections [1], radiationless relaxation of excited electronic states [2], and intra- and intermolecular electron and proton transfer [3], to name a few. The standard way of studying and interpreting these so-called, "nonadiabatic" processes is to expand the full molecular wave function in terms of the BO electronic states. Within this expansion, nonadiabatic processes can be viewed as a nuclear wave packet with contributions on several BOPESs, coupled through the nonadiabatic coupling terms which in turn induce transitions between the BOPESs. While this provides a formally exact description one may nevertheless ask: Is it also possible to study the molecular process using a *single* potential energy surface? This question is particularly relevant if one thinks of a classical or semiclassical treatment of the nuclei where a well-defined single classical force would be highly desirable.

In a recent Letter, we have introduced an exact time-dependent potential energy surface (TDPES) that, together with an exact time-dependent vector potential, governs the nuclear motion. These concepts emerge from a novel way to approach the coupled electron-nuclear dynamics via an exact factorization of the electron-nuclear wave function [4]. Features of the exact TDPES were studied in the presence of strong laser fields [4,5]. In the present Letter we investigate the generic features of the exact TDPES *without* an external laser but in the presence of strong nonadiabatic couplings. A major result will be that the exact TDPES exhibits nearly discontinuous steps connecting different static BOPES, reminiscent of Tully's surface hopping [6] in the classical limit.

In [4] we have proved that the *exact* solution of the time-dependent Schrödinger equation (TDSE), $\hat{H}\Psi(\underline{\underline{\mathbf{r}}}, \underline{\underline{\mathbf{R}}}, t) = i\partial_t\Psi(\underline{\underline{\mathbf{r}}}, \underline{\underline{\mathbf{R}}}, t)$, of the complete system of interacting electrons and nuclei can be written as $\Psi(\underline{\underline{\mathbf{r}}}, \underline{\underline{\mathbf{R}}}, t) = \Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}}, t)\chi(\underline{\underline{\mathbf{R}}}, t)$, with the nuclear wave function $\chi(\underline{\underline{\mathbf{R}}}, t)$ and the electronic conditional wave function $\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}}, t)$ that satisfies the partial normalization condition $\int d\underline{\underline{\mathbf{r}}}|\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}}, t)|^2 = 1$. In the absence of time-dependent external fields, the system is described by the Hamiltonian $\hat{H} = \hat{H}_{\mathrm{BO}}(\underline{\underline{\mathbf{r}}}, \underline{\underline{\mathbf{R}}}) + \hat{T}_n(\underline{\underline{\mathbf{R}}})$, where $\hat{H}_{\mathrm{BO}}(\underline{\underline{\mathbf{r}}}, \underline{\underline{\mathbf{R}}})$ is the traditional BO electronic Hamiltonian, and $\hat{T}_n(\underline{\underline{\mathbf{R}}})$ is the nuclear kinetic energy. Throughout this Letter we use atomic units and the electronic and nuclear coordinates are collectively denoted by $\underline{\underline{\mathbf{r}}}$ and $\underline{\underline{\mathbf{R}}}$, respectively. The exact electronic wave function satisfies the equation $(\hat{H}_{\mathrm{el}} - \epsilon(\underline{\underline{\mathbf{R}}}, t))\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}}, t) = i\partial_t\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}}, t)$, where $\hat{H}_{\mathrm{el}}(\underline{\underline{\mathbf{r}}}, \underline{\underline{\mathbf{R}}}) = \hat{H}_{\mathrm{BO}}(\underline{\underline{\mathbf{r}}}, \underline{\underline{\mathbf{R}}}) + \sum_{\nu=1}^{N_n}[(-i\nabla_\nu - \mathbf{A}_\nu(\underline{\underline{\mathbf{R}}}, t))^2/2 + (-i\nabla_\nu\chi/\chi + \mathbf{A}_\nu(\underline{\underline{\mathbf{R}}}, t))(-i\nabla_\nu - \mathbf{A}_\nu(\underline{\underline{\mathbf{R}}}, t))]/M_\nu$. Here $\{M_1, \ldots, M_{N_n}\}$ are the nuclear masses of a system with N_n nuclei. The time evolution of the nuclear wave function is governed by the Schrödinger equation:

$$\left(\sum_{\nu=1}^{N_n}\frac{(-i\nabla_\nu + \mathbf{A}_\nu(\underline{\underline{\mathbf{R}}}, t))^2}{2M_\nu} + \epsilon(\underline{\underline{\mathbf{R}}}, t)\right)\chi(\underline{\underline{\mathbf{R}}}, t) = i\partial_t\chi(\underline{\underline{\mathbf{R}}}, t). \tag{1}$$

The TDPES appearing in this equation is defined as $\epsilon(\underline{\underline{\mathbf{R}}}, t) = \langle\Phi_{\underline{\underline{\mathbf{R}}}}(t)|\hat{H}_{\mathrm{el}}(\underline{\underline{\mathbf{r}}}, \underline{\underline{\mathbf{R}}}) - i\partial_t|\Phi_{\underline{\underline{\mathbf{R}}}}(t)\rangle_{\underline{\underline{\mathbf{r}}}}$, and the vector

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potential is given by $\mathbf{A}_\nu(\underline{\underline{\mathbf{R}}}, t) = \langle \Phi_{\underline{\underline{\mathbf{R}}}}(t) | -i\nabla_\nu \Phi_{\underline{\underline{\mathbf{R}}}}(t)\rangle_{\underline{\underline{\mathbf{r}}}}$. $\epsilon(\underline{\underline{\mathbf{R}}}, t)$ is a sum of two parts, the gauge-invariant [7] term

$$\epsilon_{\mathrm{gi}}(\underline{\underline{\mathbf{R}}}, t) = \langle \Phi_{\underline{\underline{\mathbf{R}}}}(t) | \hat{H}_{\mathrm{el}}(\underline{\underline{\mathbf{r}}}, \underline{\underline{\mathbf{R}}}) | \Phi_{\underline{\underline{\mathbf{R}}}}(t)\rangle_{\underline{\underline{\mathbf{r}}}}, \tag{2}$$

and a gauge-dependent one given by

$$\epsilon_{\mathrm{gd}}(\underline{\underline{\mathbf{R}}}, t) = \langle \Phi_{\underline{\underline{\mathbf{R}}}}(t) | -i\partial_t | \Phi_{\underline{\underline{\mathbf{R}}}}(t)\rangle_{\underline{\underline{\mathbf{r}}}}. \tag{3}$$

Here, $\langle \cdots | \cdots | \cdots \rangle_{\underline{\underline{\mathbf{r}}}}$ denotes the inner product over electronic variables only.

Why is this representation of the correlated electron-nuclear many-body problem exciting? The wave function $\chi(\underline{\underline{\mathbf{R}}}, t)$ that satisfies the exact nuclear equation of motion (1) leads to an N-body density $\Gamma(\underline{\underline{\mathbf{R}}}, t) = |\chi(\underline{\underline{\mathbf{R}}}, t)|^2$ and an N-body current density $\mathbf{J}_\nu(\underline{\underline{\mathbf{R}}}, t) = \mathrm{Im}(\chi^* \nabla_\nu \chi) + \Gamma(\underline{\underline{\mathbf{R}}}, t)\mathbf{A}_\nu$ which reproduce the true nuclear N-body density and current density obtained from the full wave function $\Psi(\underline{\underline{\mathbf{r}}}, \underline{\underline{\mathbf{R}}}, t)$ [5]. In this sense, $\chi(\underline{\underline{\mathbf{R}}}, t)$ can be viewed as the proper nuclear wave function. The time evolution of $\chi(\underline{\underline{\mathbf{R}}}, t)$, on the other hand, is completely determined by the TDPES and the vector potential. Moreover, these potentials are *unique* up to within a gauge transformation. This uniqueness is straightforwardly proven by following the steps of the current-density version [8] of the Runge-Gross theorem [9]. In other words, if one wants a TDSE whose solution $\chi(\underline{\underline{\mathbf{R}}}, t)$ yields the true nuclear N-body density and current density, then the potentials appearing in this TDSE are (up to within a gauge transformation) uniquely given by $\mathbf{A}_\nu(\underline{\underline{\mathbf{R}}}, t)$ and $\epsilon(\underline{\underline{\mathbf{R}}}, t)$; there is no other choice. This also implies that the gradient of this exact TDPES is the only correct force on the nuclei in the classical limit (plus terms arising from the vector potential, if those cannot be gauged away). The goal of this Letter is to find out how this exact TDPES looks when one has strong nonadiabatic couplings in the traditional expansion in BO states. One major result will be that the exact TDPES shows nearly discontinuous steps whenever the nuclear wave packet splits in the vicinity of an avoided crossing of the BOPES.

To study the exact TDPES we first of all need a problem that is simple enough to allow for a numerically exact solution and that nevertheless exhibits the characteristic features associated with strong nonadiabatic couplings, such as the splitting of the nuclear wave packet. For this purpose we employ the model of Shin and Metiu [10]. It consists of three ions and a single electron. Two ions are fixed at a distance of $L = 19.0a_0$, the third ion and the electron are free to move in one dimension along the line joining the two fixed ions. The Hamiltonian of this system reads

$$\begin{aligned}\hat{H}(r, R) = {}& -\frac{1}{2}\frac{\partial^2}{\partial r^2} - \frac{1}{2M}\frac{\partial^2}{\partial R^2} + \frac{1}{|\frac{L}{2} - R|} + \frac{1}{|\frac{L}{2} + R|} \\ & - \frac{\mathrm{erf}\left(\frac{|R-r|}{R_f}\right)}{|R - r|} - \frac{\mathrm{erf}\left(\frac{|r-\frac{L}{2}|}{R_r}\right)}{|r - \frac{L}{2}|} - \frac{\mathrm{erf}\left(\frac{|r+\frac{L}{2}|}{R_l}\right)}{|r + \frac{L}{2}|}.\end{aligned} \tag{4}$$

Here, the symbols $\underline{\underline{\mathbf{r}}}$ and $\underline{\underline{\mathbf{R}}}$ are replaced by r and R, the coordinates of the electron and the movable nucleus measured from the center of the two fixed ions. $M = 1836$ a.u. and we choose $R_f = 5.0a_0$, $R_l = 3.1a_0$, and $R_r = 4.0a_0$ such that the first BOPES $\epsilon_{\mathrm{BO}}^{(1)}$ is strongly coupled to the second BOPES $\epsilon_{\mathrm{BO}}^{(2)}$ around the avoided crossing at $R_{\mathrm{ac}} = -1.90a_0$ and there is a weak coupling to the rest of the surfaces. The first three BOPESs are shown in Fig. 1, together with the BO conditional electronic densities $|\phi_R^{(1)}(r)|^2$ and $|\phi_R^{(2)}(r)|^2$. As expected, $|\phi_R^{(1)}(r)|^2$ and $|\phi_R^{(2)}(r)|^2$ exhibit abrupt changes, along the R axis, at the position of the avoided crossing, R_{ac}: $|\phi_R^{(1)}(r)|^2$ switches from being localized around the fixed ion on the left ($r = -9.5a_0$), to be localized around the one on the right ($r = 9.5a_0$); $|\phi_R^{(2)}(r)|^2$ on the other hand, presents a single-peak structure for $R < R_{\mathrm{ac}}$ and a double-peak structure for $R > R_{\mathrm{ac}}$.

We suppose that the system is initially excited to $\epsilon_{\mathrm{BO}}^{(2)}$ and the initial nuclear wave function is a wave packet with the width $\sigma = 1/\sqrt{2.85}$, centered at $R = -4.0a_0$ (see Fig. 1, black solid line); i.e., the initial full wave function is $\Psi_0(r, R) = Ae^{-(R-4)^2/\sigma^2}\phi_R^{(2)}(r)$ with A being a normalization constant. Starting with $\Psi_0(r, R)$ as the initial state, we propagate the TDSE, numerically exactly, to obtain the full molecular wave function $\Psi(r, R, t)$ and from it we calculate, as discussed in Ref. [5] (see also the Supplemental Material [11]), the TDPES in the gauge where the vector

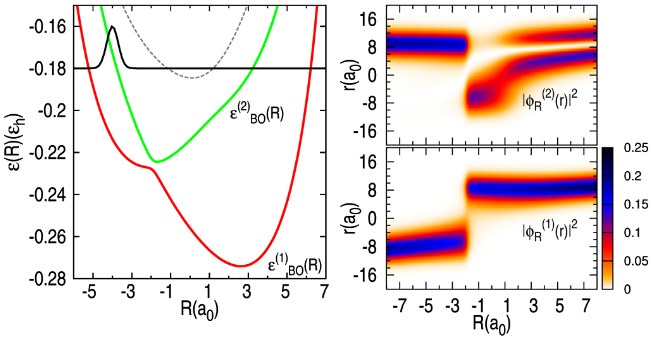

FIG. 1 (color online). Left: The first two BOPESs (indicated in the figure) together with the third BOPES (black dashed line) and the initial nuclear wave function (black solid line). Right: Adiabatic electronic conditional densities as indicated in the figures: the x axis represents the parametric coordinate R, the y axis is the electronic coordinate r, and along the z axis we plot the conditional probability of finding the electron in r given that the ion is in R.

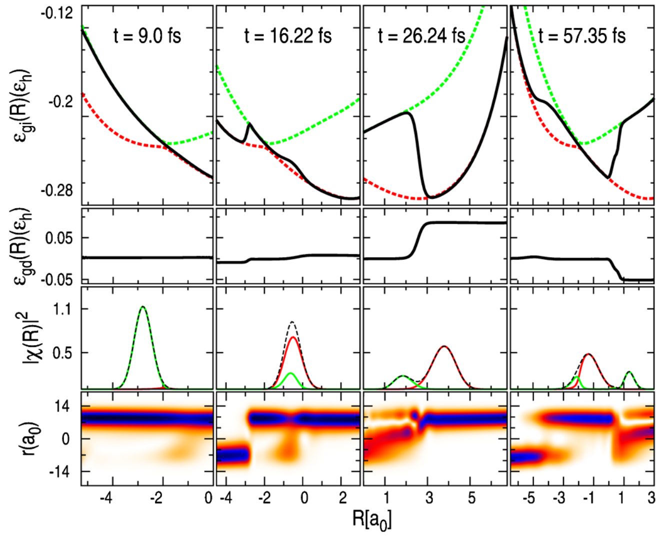

FIG. 2 (color online). First panel (top): The gauge independent part of the TDPES (black solid line) plotted at four different times (indicated), $\epsilon_{\mathrm{BO}}^{(1)}$ (red or dark gray dashed line), and $\epsilon_{\mathrm{BO}}^{(2)}$ (green or light gray dashed line). Second panel (from the top): The gauge-dependent part of the TDPES is plotted at the same times. Third panel (from the top): The exact nuclear density (black dashed line) is shown together with $|F_1(R,t)|^2$ (red or dark gray solid line) and $|F_2(R,t)|^2$ (green or light gray solid line). Lowest panel: The exact time-dependent electronic conditional density $|\Phi_R(r,t)|^2$ is plotted. The color range is the same as Fig. 1.

potential is zero. Hence, the TDPES is the only potential acting on the nuclear subsystem. In the upper panel of Fig. 2, the gauge-invariant part of the TDPES (2) ϵ_{gi} is plotted (black solid line) at four different times, along with the two lowest BOPESs, $\epsilon_{\mathrm{BO}}^{(1)}$ (red or dark gray dashed line) and $\epsilon_{\mathrm{BO}}^{(2)}$ (green or light gray dashed line). In the second panel (from the top), the gauge-dependent part of the TDPES (3) ϵ_{gd} is plotted at the same times. In the third panel (from the top), the exact nuclear density (black dashed line) $|\chi(R,t)|^2$ is shown together with the absolute value squared of the projection of the full wave function on the first and second BO electronic states, i.e., $|F_1(R,t)|^2 = |\int dr \phi_R^{(1)*}(r)\Psi(r,R,t)|^2$ (red or dark gray solid line) and $|F_2(R,t)|^2 = |\int dr \phi_R^{(2)*}(r)\Psi(r,R,t)|^2$ (green or light gray solid line). In the lowest panel, $|\Phi_R(r,t)|^2$ is presented.

At the initial time ($t = 0$), due to the choice of the initial state, the TDPES coincides with $\epsilon_{\mathrm{BO}}^{(2)}$. Since $\Psi_0(r,R)$ is not an eigenstate of the Hamiltonian (4), it evolves in time. At $t = 9.0$ fs, ϵ_{gi} coincides with $\epsilon_{\mathrm{BO}}^{(2)}$ for $R < R_{\mathrm{ac}}$, goes smoothly through the avoided crossing region, and follows $\epsilon_{\mathrm{BO}}^{(1)}$ for $R > R_{\mathrm{ac}}$, resembling the *diabatic* potential energy surface of state 2 in Ref. [10], in which the electron interacts with the fixed ion on the right ($r = 9.5a_0$) and with the moving ion, but not with the fixed ion on the left ($r = -9.5a_0$). As ϵ_{gd} is constant in this region (Fig. 2), the TDPES is identical with ϵ_{gi} [12]. The nuclear wave packet is driven by the TDPES to spread toward the avoided crossing of two BOPESs, where a significant nonadiabatic transition happens and the exact nuclear density splits. Already at this moment, a slight transition of the nuclear wave packet to the lower surface is visible around the avoided crossing. At later times, e.g., $t = 16.22$, $t = 26.24$, and $t = 57.35$ fs, far from the avoided crossing, ϵ_{gi} contains steps that connect its different pieces that are on top of different BOPESs in different slices of R space. In the region around R_{ac}, it follows the diabatic surface that passes smoothly through the avoided crossing. On the other hand, ϵ_{gd} is piecewise constant and presents similar steps as ϵ_{gi}. Therefore, the TDPES $\epsilon_{\mathrm{gi}} + \epsilon_{\mathrm{gd}}$ preserves the features mentioned before: i.e., (i) far from the avoided crossing, it presents steps that connect the regions in R space in which the TDPES has the shape of one BOPES to the regions in which it has the shape of the other BOPES; (ii) around the avoided crossing, it follows the diabatic surface that smoothly connects one BOPES to the other.

The exact TDPES represented in Fig. 2 can be viewed from a different perspective. The nuclear wave packet from a semiclassical point of view can be represented as an ensemble of classical trajectories, along which point particles evolve under the action of a classical force which is the gradient of ϵ_{gi}. According to our observations, on different sides of a step such a force is calculated from different BOPESs. This is reminiscent of Tully's surface hopping approach [6,13], that deals with the problem of coupled electron-nuclear dynamics semiclassically. The method introduces stochastic jumps between BOPESs to select the adiabatic surface that, at each point in time, governs the classical nuclear dynamics. The nuclear density is reconstructed from *bundles* of classical trajectories. Such bundles evolve independently from one another on different adiabatic surfaces and are a semiclassical approximation of the components $|F_k(R,t)|^2$ of the exact nuclear density. The step feature of the TDPES, following from the exact solution of the full TDSE, makes clear that, after the wave packet splits at the avoided crossing, the motion of its components (the bundles in surface hopping language) is driven by single adiabatic surfaces and not (like, e.g., in Ehrenfest dynamics) by an average electronic potential.

The exact time-dependent electronic conditional density, shown in the lower panels of Fig. 2 at different times, behaves similarly to the TDPES: (i) it smoothly connects a $|\phi_R^{(2)}(r)|^2$-like structure, by crossing R_{ac}, with a $|\phi_R^{(1)}(r)|^2$-like structure, or vice versa, presenting a diabatic behavior, e.g., at $t = 9.0$ fs; (ii) it displays abrupt changes between regions that piecewise match different adiabatic conditional densities.

In order to analyze the behavior of the TDPES, we rewrite it by expanding the exact electronic conditional wave function in terms of the adiabatic electronic states [5]. Because of the choice of the parameter in the Hamiltonian, we only need to include the first two BO states, then $\Phi_R(r,t) = C_1(R,t)\phi_R^{(1)}(r) + C_2(R,t)\phi_R^{(2)}(r)$. We expand the full electron-nuclear wave function in the same basis, $\Psi(r,R,t) = F_1(R,t)\phi_R^{(1)}(r) + F_2(R,t)\phi_R^{(2)}(r)$, where the expansion coefficients, F_k's and C_k's, are related as

$$C_k(R,t) = \frac{F_k(R,t)}{\chi(R,t)} = \frac{e^{-i\theta(R,t)}F_k(R,t)}{\sqrt{|F_1(R,t)|^2 + |F_2(R,t)|^2}}. \qquad (5)$$

Here, θ is the phase of the exact nuclear wave function and we have used the relation $|\chi(R,t)|^2 = |F_1(R,t)|^2 + |F_2(R,t)|^2$, determined by $\int dr|\Psi(r,R)|^2$. Now, we may rewrite $\epsilon_{\rm gi}(R,t)$ and $\epsilon_{\rm gd}(R,t)$ in terms of $\epsilon_{\rm BO}^{(k)}(R)$ and $C_k(R,t)$ $(k = 1, 2)$:

$$\epsilon_{\rm gi}(R,t) = \sum_{k=1,2} |C_k(R,t)|^2 \epsilon_{\rm BO}^{(k)}(R), \qquad (6)$$

$$\epsilon_{\rm gd}(R,t) = \sum_{k=1,2} |C_k(R,t)|^2 \dot{\gamma}_k(R,t), \qquad (7)$$

where γ_1 and γ_2 are the phases of C_1, C_2. In Eq. (6), all terms of $\mathcal{O}(M^{-1})$ have been neglected and it only contains BOPESs which are the leading terms responsible for the shape of $\epsilon_{\rm gi}(R,t)$, especially far from the avoided crossing where the nonadiabatic couplings are small. The gauge-dependent term is written in terms of the time derivative of the phases, $\dot{\gamma}_1$ and $\dot{\gamma}_2$. $|C_1|^2$ and $|C_2|^2$ vary between 0 and 1 and $|C_1|^2 + |C_2|^2 = 1$ by virtue of the partial normalization condition. Therefore, as Eq. (6) suggests, in the region where $\epsilon_{\rm gi}(R,t)$ coincides with $\epsilon_{\rm BO}^{(1)}(R)$, the corresponding expansion coefficient $|C_1|^2$ is close to 1 while $|C_2|^2$ is close to 0 and vice versa. We have observed [Eq. (5)] that at R_0, the crossover of $|F_1|$ and $|F_2|$ where $|F_1(R_0,t)| = |F_2(R_0,t)| = |X(t)|$, $|C_1|^2$ and $|C_2|^2$ are always equal to $\frac{1}{2}$ and R_0 is the center of the region where steps form. Moving away from this point, one of the $|C_k|^2$'s becomes dominant (Fig. 3) and $\epsilon_{\rm gi}(R,t)$ lies on top of the corresponding BOPES.

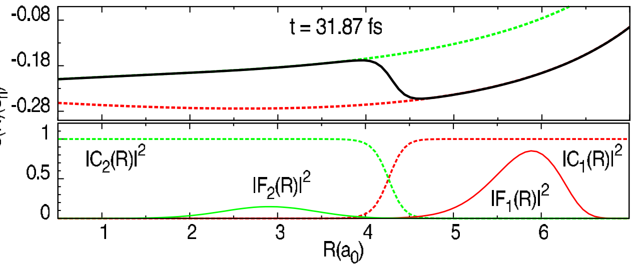

FIG. 3 (color online). Top: A snapshot of the gauge-invariant part of the TDPES (solid black line) at the $t = 31.87$ fs. For reference, $\epsilon_{\rm BO}^{(1)}$ (red or dark gray dashed line) and $\epsilon_{\rm BO}^{(2)}$ (green or light gray dashed line) are shown. Bottom: Expansion coefficients (indicated in the figure) of the (two states) adiabatic expansion of the full wave function and the exact electronic conditional wave function (see the text) at $t = 31.87$ fs.

To elaborate on how the TDPES switches between the two adiabatic states, we Taylor expand $|C_k(R,t)|^2$ around R_0 and keep only up to the linear order terms: $|C_{\substack{1\\2}}(R,t)|^2 = [1 \pm \alpha(t)(R - R_0)]/2$, where $\alpha(t) = [(\nabla_R|F_1(R,t)|)_{R_0} - (\nabla_R|F_2(R,t)|)_{R_0}]/|X(t)|$. Now, using the relation $0 \le |C_k|^2 \le 1$ $(k = 1, 2)$, we can estimate the width of the region ΔR where the switching between BOPESs occurs as $2/\alpha$. Hence, the larger the values of α, the sharper the steps become.

As an example, we discuss the TDPES at $t = 31.87$ fs in Fig. 3. As it is seen, $\epsilon_{\rm gi}$ switches from $\epsilon_{\rm BO}^{(1)}(R)$ to $\epsilon_{\rm BO}^{(2)}(R)$ over the region where $|F_1|$ and $|F_2|$ cross (see the bottom plot). As $|F_1|$ and $|F_2|$ have opposite slopes and cross where they are small, α is large yielding a small ΔR. Outside the switching region, one of the $|C_k|^2$s becomes dominant (see also the Supplemental Material [11] for more details).

The concept of TDPES developed in [4] is completely general. In [4] the TDPES of H_2^+ in strong laser fields were used to identify different mechanisms of dissociation. We expect interesting insights also in resonant processes such as photochemistry on conducting surfaces or resonance-mediated inelastic transport from the study of the corresponding TDPES. In this Letter, we have presented generic features of the exact TDPES for the specific situation where, according to the standard BO expansion framework, significant nonadiabatic transitions occur and the nuclear wave packet splits at the avoided crossing of two BOPESs. For the one-dimensional model system studied here, the TDPES is the only potential that governs the dynamics of the nuclear wave function (the vector potential can be gauged away) and provides us with an alternative way of visualizing and interpreting the nonadiabatic processes. We have shown that the gauge-invariant part of the TDPES $\epsilon_{\rm gi}(R,t)$ is characterized by two generic features: (i) in the vicinity of the avoided crossing, $\epsilon_{\rm gi}(R,t)$ becomes identical with a diabatic potential energy surface in the direction of the wave-packet motion; (ii) far from the avoided crossing, $\epsilon_{\rm gi}(R,t)$, as a function of R, is piecewise identical with different BOPESs and exhibits nearly discontinuous steps in between. The latter feature holds after the wave packet branches and leaves the avoided crossing. The gauge-dependent part $\epsilon_{\rm gd}(R,t)$, on the other hand, is piecewise constant in the region where $\epsilon_{\rm gi}(R,t)$ coincides with different BOPESs. Hence, $\epsilon_{\rm gd}(R,t)$ has little effect on the gradient of the total TDPES, but may shift the BOPES pieces of $\epsilon_{\rm gi}(R,t)$ by different constants causing the exact TDPES to be piecewise parallel to the BOPESs. The diabatic feature (i) of the TDPES supports the use of diabatic surfaces as the driving potential when a wave packet approaches a region of strong nonadiabatic coupling. The step feature (ii) is in agreement with the semiclassical picture of nonadiabatic nuclear dynamics provided by the Tully's surface hopping scheme, which suggests we calculate the classical forces acting on the nuclei according to the gradient of only one of the BOPESs. While our findings are based on a simple model for which the TDSE can be integrated numerically exactly, we expect that the diabatic shape and the steps are generic features occurring as well in large realistic systems. Clearly, systems with many degrees of freedom will require the introduction of approximations. We expect that the concepts developed in this Letter will ultimately lead to improved algorithms for the mixed quantum-classical treatment of electrons and nuclei.

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