Steps 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 non-adiabatic 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 1D 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 (PES) generated by the electrons in a specific electronic eigenstate. The BO approximation breaks down when two or more BOPESs 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], intra- and inter-molecular electron and proton transfer [3], to name a few. The standard way of studying and interpreting these, so-called, “non-adiabatic” processes is to expand the full molecular wave function in terms of the BO electronic states. Within this expansion, non-adiabatic processes can be viewed as a nuclear wave packet with contributions on several BOPESs, coupled through the non-adiabatic coupling (NAC) 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 PES? This question is particularly relevant if one thinks of a classical or semi-classical 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 (TD PES) that, together with an exact time-dependent vector potential govern 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 TD PES were studied in the presence of strong laser fields [4,5]. In the present Letter we investigate the generic features of the exact TD PES without external laser but in the presence of strong non-adiabatic couplings. A major result will be that the exact TD PES exhibits nearly discontinuous steps connecting different static BOPESs, 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),

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

of the complete system of interacting electrons and nuclei can be written as a single product (unlike the BO expansion), \( \Psi(\mathbf{r}, \mathbf{R}, t) = \Phi_R(\mathbf{r}, t) \chi(\mathbf{R}, t) \), of the nuclear wave-function, \( \chi(\mathbf{R}, t) \), and the electronic conditional wave-function, \( \Phi_R(\mathbf{r}, t) \), that satisfies the partial normalization condition (PNC), \( \int d\mathbf{r} |\Phi_R(\mathbf{r}, t)|^2 = 1 \). In the absence of time-dependent external fields, the system is described by the Hamiltonian \( \hat{H} \),

\[ \hat{H} = \hat{H}_{BO}(\mathbf{r}, \mathbf{R}) + \tilde{T}_n(\mathbf{R}), \]

that contains the traditional BO electronic Hamiltonian, \( \hat{H}_{BO}(\mathbf{r}, \mathbf{R}) = \tilde{T}_e(\mathbf{r}) + W_{ee}(\mathbf{r}) + V_{en}(\mathbf{r}, \mathbf{R}) + W_{nn}(\mathbf{R}) \), and the nuclear kinetic energy, \( \tilde{T}_n(\mathbf{R}) \). Throughout this paper we use atomic units (unless stated otherwise) and the electronic and nuclear coordinates are collectively denoted by \( \mathbf{r} \) and \( \mathbf{R} \), respectively.

The exact electronic wave-function satisfies the equation

\[ \left( \hat{H}_{BO}(\mathbf{r}, \mathbf{R}) + \hat{U}^{\text{coup}} - \epsilon(\mathbf{R}, t) \right) \Phi_R(\mathbf{r}, t) = i \partial_t \Phi_R(\mathbf{r}, t), \]

where the electron-nuclear coupling operator is

\[ \hat{U}^{\text{coup}} = \sum_{\nu=1}^{N_e} \left( -i \nabla_{\nu} - A_{\nu}(\mathbf{R}, t) \right)^2 / 2 + \left( -i \nabla_{\nu} \chi / \chi + A_{\nu}(\mathbf{R}, t) \right) / M_{\nu}. \]

The time-evolution of the nuclear wave-function is governed by the Schrödinger equation:

\[ \sum_{\nu=1}^{N_n} \left( -i \nabla_{\nu} + A_{\nu}(\mathbf{R}, t) \right)^2 / 2M_{\nu} + \epsilon(\mathbf{R}, t) \chi(\mathbf{R}, t) = i \partial_t \chi(\mathbf{R}, t). \]
These equations lead to rigorous definitions of the TDPES and the time-dependent vector potential

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

$$A_{\nu}(R, t) = \left\langle \Phi_{R}(t) \right| -i\nabla_{\nu} \Phi_{R}(t) \right\rangle.$$  

(5)

The TDPES consists of two parts: $\epsilon_{gi}(R, t)$, defined as

$$\epsilon_{gi}(R, t) = \left\langle \Phi_{R}(t) \right| \hat{H}_{BO}(r, R) + \hat{\mathcal{F}}_{\text{en}}(r, R, t) \left| \Phi_{R}(t) \right\rangle,$$

is form-invariant under the gauge-transformation

$$\Phi_{R}(r, t) \rightarrow \tilde{\Phi}_{R}(r, t) = \exp(i\theta(R, t))\Phi_{R}(r, t),$$

$$\chi(R, t) \rightarrow \tilde{\chi}(R, t) = \exp(-i\theta(R, t))\chi(R, t),$$

whereas

$$\epsilon_{gd}(R, t) = \left\langle \tilde{\chi}_{\nu}(R, t) \right| -i\partial_{\nu} \tilde{\Phi}_{R}(t) \right\rangle,$$

(8)

is the part that depends on the choice of the gauge. Here, $\left\langle ... \right\rangle_{\xi}$ denotes an inner product over the electronic variables only.

Why is this representation of the correlated electron-nuclear many-body problem exciting? The wavefunction $\chi(R, t)$ that satisfies the exact nuclear equation of motion [1] leads to an $N$-body density $\Gamma(R, t) = |\chi(R, t)|^2$ and an $N$-body current density $J_{\nu}(R, t) = i\hat{M}(\chi^* \nabla_{\nu} \chi) + \Gamma^{\mu}(R, t)A_{\nu}$ which reproduce the true nuclear $N$-body density and current density obtained from the full wave-function $\Psi(r, R, t)$ [5]. In this sense, $\chi(R, t)$, can be viewed as the proper nuclear wavefunction. The time evolution of $\chi(R, t)$, on the other hand, is completely determined by the TDPES, $\epsilon(R, t)$, and the vector potential, $A_{\nu}(R, t)$. 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 [6] of the Runge-Gross theorem [7]. In other words, if one wants a TDSE [4] whose solution $\chi(R, t)$ 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 Eqs. (5,8), 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 like when one has strong non-adiabatic couplings in the traditional expansion in BO states. One major result will be that the exact TDPES shows a nearly discontinuous step whenever the nuclear wave-packet splits in the vicinity of an avoided crossing of the BOPES.

To study the exact TDSE 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 non-adiabatic couplings, such as the splitting of the nuclear wave packet.

For this purpose we employ the model of Shin and Metiu [8]. It consists of three ions and a single electron. Two ions are fixed at a distance of $L = 19.0 \text{ a}_0$, 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

$$\hat{H}(r, R) = -\frac{1}{2}\frac{\partial^2}{\partial r^2} - \frac{1}{2}\frac{\partial^2}{\partial R^2} + \frac{1}{|\frac{1}{2} - R|} + \frac{1}{|\frac{1}{2} + R|} - \text{erf} \left( \frac{|R - r|}{R_f} \right) - \text{erf} \left( \frac{|r - \frac{1}{2}|}{R_c} \right) - \text{erf} \left( \frac{|r + \frac{1}{2}|}{R_c} \right),$$

(9)

Here, the symbols $r$ and $R$ 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 $R_f = 5.0 \text{ a}_0$, $R_l = 3.1 \text{ a}_0$ and $R_c = 4.0 \text{ a}_0$ such that the first BOPES, $\epsilon_{BO}^{(1)}$, is strongly coupled to the second BOPES, $\epsilon_{BO}^{(2)}$, around the avoided crossing at $R_{ac} = -1.90 \text{ a}_0$ and there is a weak coupling to the rest of the surfaces. The first three BOPES are shown in Fig. 1 (left panel), together with the BO conditional electronic densities $|\phi_{R}^{(1)}(r)|^2$ and $|\phi_{R}^{(2)}(r)|^2$ (right panels). As expected, $|\phi_{R}^{(1)}(r)|^2$ exhibit abrupt changes, along the $R$-axis, at the position of the avoided crossing, $R_{ac}$; $|\phi_{R}^{(2)}(r)|^2$ switches from being localized around the fixed ion on the left ($r = -9.5 \text{ a}_0$), to be localized around the one on the right ($r = 9.5 \text{ a}_0$); $|\phi_{R}^{(2)}(r)|^2$ on the other hand, presents a single-peak structure for $R < R_{ac}$ and a double-peak structure for $R > R_{ac}$.

We suppose that the system is initially excited to $\epsilon_{BO}^{(2)}$ and the initial nuclear wave-function is a wave-packet with the width $\sigma = 1/\sqrt{2.85}$, centered at $R = -4.0 \text{ a}_0$ (see Fig. 1 black solid-line), i.e., the initial full wave-function is $\Psi_0(r, R) = A e^{-\frac{(R - 4)^2}{2\sigma^2}} \phi_{R}^{(2)}(r)$ with $A$ being a normalization constant. Starting with $\Psi_0(r, R)$ as initial state, we propagate the TDSE, nu-
FIG. 2. First panel (top): The gauge independent part of the TDPES (black solid-line) plotted at four different times (indicated), $\epsilon_{\text{gd}}^{(1)}$ (red dashed-line) and $\epsilon_{\text{gd}}^{(2)}$ (green 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 solid-line) is shown together with $|F_{1}(R, t)|^2$ (red solid-line) and $|F_{2}(R, t)|^2$ (green solid-line). Lowest panel: the exact time-dependent electronic conditional density, $|\Psi_{R}(r, t)|^2$, is plotted. The color range is the same as Fig. 1.

Numerically exactly, to obtain the full molecular wave function $\Psi(r, R, t)$ and from it we calculate, as discussed in Ref. [5], the TDPES in the gauge where the vector potential is zero. Hence, the TDPES is the only potential acting on the nuclear sub-system. In the upper panel of Fig. 2 the gauge-invariant part of the TDPES $\epsilon_{\text{gi}}$, is plotted (black solid-line) at four different times, along with the two lowest BOPESs, $\epsilon_{\text{BO}}^{(1)}$ (red dashed-line) and $\epsilon_{\text{BO}}^{(2)}$ (green dashed-line). In the second panel (from the top), the gauge-dependent part of the TDPES $\epsilon_{\text{gd}}$, 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 solid-line) and $|F_{2}(R, t)|^2 = \int dr \phi_{R}^{(2)*}(r)\Psi(r, R, t)|^2$ (green solid-line). In the lowest panel, $|\Psi_{R}(r, t)|^2$ is presented.

At the initial time ($t = 0$), due to the choice of the initial state, the TDPES coincides with $\epsilon_{\text{BO}}^{(2)}$. Since $\Psi_{0}(r, R)$ is not an eigenstate of the Hamiltonian [7], it evolves in time. At $t = 9.0 \text{ fs}$, $\epsilon_{\text{gi}}$ coincides with $\epsilon_{\text{BO}}^{(2)}$ for $R < R_{\text{ac}}$, goes smoothly through the avoided crossing region and follows $\epsilon_{\text{BO}}^{(1)}$ for $R > R_{\text{ac}}$, resembling the diabatic PES of state 2 in Ref. [8], in which the electron interacts with the fixed ion on the right ($r = -9.5 \ a_{0}$) and with the moving ion, but not with the fixed ion on the left ($r = -9.5 \ a_{0}$). As $\epsilon_{\text{gd}}$ is constant in this region (Fig. 2), the TDPES is identical with $\epsilon_{\text{gi}}$ [9]. The nuclear wave-packet is driven by the TDPES to spread towards the avoided crossing of two BOPESs, where a significant non-adiabatic 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., $t = 16.22 \ f s$, $t = 26.24 \ f s$ and $t = 57.35 \ f s$, far from the avoided crossing, $\epsilon_{\text{gi}}$ contains steps that connect its different pieces that are on top of different BOPESs in different slices of $R$-space. In the region around $R_{\text{ac}}$, it follows the diabatic surface that passes smoothly through the avoided crossing. On the other hand, $\epsilon_{\text{gd}}$ is piecewise constant and presents similar steps as $\epsilon_{\text{gi}}$. Therefore, the TDPES, $\epsilon_{\text{gi}} + \epsilon_{\text{gd}}$, 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 semi-classical 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 $\epsilon_{\text{gi}}$. According to our observations, on different sides of a step such a force is calculated from different BOPESs. This is reminiscent of the *jumping between the adiabatic surfaces* in algorithms such as Tully’s surface hopping [10, 11]. However, while Tully surface hopping is a stochastic algorithm, the jumps in the exact TDPES correspond to an exact solution of the TDSE. When the time-dependent vector potential can not be set to zero, a gauge can be chosen in which $\epsilon_{\text{gd}}$ is zero and a time-dependent vector potential together with $\epsilon_{\text{gi}}$ specifies the classical force that the nuclei experience in different slices of $R$-space. Investigating $\epsilon_{\text{gi}}$ together with the time-dependent vector potential for a wide range of situations may help to improve the existing semi-classical procedures to simulate non-adiabatic nuclear dynamics.

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 $R_{\text{ac}}$, with a $|\phi_{R}^{(1)}(r)|^2$-like structure, or vice versa, presenting a diabatic behavior, e.g. at $t = 9.0 \ f s$; (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.
Due to the choice of the parameter in the Hamiltonian, we only need to include the first two BO states, then

$$\Phi_R(r,t) = C_1(R,t)\phi_R^{(1)}(r) + C_2(R,t)\phi_R^{(2)}(r). \quad (10)$$

We expand the full electron-nuclear wave-function in the same basis,

$$\Psi(r,R,t) = F_1(R,t)\phi_R^{(1)}(r) + F_2(R,t)\phi_R^{(2)}(r), \quad (11)$$

where the expansion coefficients, $F_k$'s and $C_k$'s, are related as

$$C_k(R,t) = \frac{F_k(R,t)}{\chi(R,t)} = \frac{e^{-i\theta(R,t)}\chi(R,t)}{\sqrt{|F_1(R,t)|^2 + |F_2(R,t)|^2}}. \quad (12)$$

Here, $\theta$ 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 $\int dr|\Psi(r,R,t)|^2$ using Eq. (11) and the orthonormality of the adiabatic states. By using Eqs. (9) and (10), we rewrite $\epsilon_{gi}(R,t)$ and $\epsilon_{gd}(R,t)$ in terms of $\epsilon_{BO}^{(1)}(R)$ and $C_k(R,t)$ ($k = 1, 2$)

$$\epsilon_{gi}(R,t) = \sum_{k=1,2} |C_k(R,t)|^2 \epsilon_{BO}^{(1)}(R) \quad (13)$$

and

$$\epsilon_{gd}(R,t) = \sum_{k=1,2} |C_k(R,t)|^2 \epsilon_{k}(R,t), \quad (14)$$

where $\gamma_1$ and $\gamma_2$ are the phases of $C_1$, $C_2$. In Eq. (13), all terms of $O(M^{-1})$ have been neglected and it only contains BOPESs which are the leading terms responsible for the shape of $\epsilon_{gi}(R,t)$, especially far from the avoided crossing where the NACs are small. The gauge-dependent term is written in terms of the time derivative of the phases, $\gamma_1$ and $\gamma_2$. $|C_1|^2$ and $|C_2|^2$ vary between 0 and 1 and $|C_1|^2 + |C_2|^2 = 1$ by virtue of the PNC. Therefore, as Eq. (13) suggests, in the region where $\epsilon_{gi}(R,t)$ coincides with $\epsilon_{BO}^{(1)}(R)$, the corresponding expansion coefficient $|C_1|^2$ is close to one while $|C_2|^2$ is close zero and vice versa. We have observed (Eq. (12)) that at $R_0$, the cross-over 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 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 $\epsilon_{gi}(R,t)$ lies on top of the corresponding BOPES.

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

$$\left|C_k(R,t)\right|^2 = |1 \pm \alpha(t) (R - R_0)| / 2, \quad (15)$$

where

$$\alpha(t) = \frac{\nabla_R |F_1(R,t)|R_0 - \nabla_R |F_2(R,t)|R_0}{|X(t)|}. \quad (16)$$

Eq. (15), using the relation $0 \leq |C_k|^2 \leq 1$ $(k = 1, 2)$ or equivalently $|R - R_0| \leq \alpha^{-1}$, estimates the width of the region, $\Delta R$, where the switching between BOPESs occurs with $\Delta R = \frac{1}{\alpha}$. Hence, the larger the values of $\alpha$, the sharper the steps become.

As an example, we discuss the TDPES at $t = 31.87 \, fs$ in Fig. 3. As it is seen, $\epsilon_{gi}$ switches from $\epsilon_{BO}^{(1)}(R)$ to $\epsilon_{BO}^{(2)}(R)$ 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, $\alpha$ is large yielding a small $\Delta R$. Outside the switching region, one of the $|C_k|^2$'s becomes dominant. Interestingly, the exact electron-nuclear density contains signatures of the behavior $\epsilon_{gi}$, i.e., where $\epsilon_{gi}$ coincides with $\epsilon_{BO}^{(1)}(R)$, presents one peak in analogy with $|\phi_R^{(1)}(r)|^2$ (see Fig. 1), while, where $\epsilon_{gi}(R,t)$ follows $\epsilon_{BO}^{(2)}(R)$, it displays two peaks, like $|\phi_R^{(2)}(r)|^2$ (Fig. 1). The step of $\epsilon_{gi}$ in the intermediate region is indicated by scars in the full electron-nuclear density.

In conclusion, we have presented generic features of the exact TDPES for situations in which, according to the standard BO expansion framework, significant non-adiabatic transitions occur and the nuclear wave-packet splits at the avoided crossing of two BOPESs. For the 1D 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 non-adiabatic processes. We have shown that the gauge-invariant part of the TDPES, $\epsilon_{gi}(R,t)$, is characterized by two generic features: (i) in the vicinity of the avoided crossing, $\epsilon_{gi}(R,t)$, be-

**FIG. 3.** Top: the full electron-nuclear density at the $t = 31.87 \, fs$. Middle: a snapshot of the gauge invariant part of the TDPES (solid black line) at the $t = 31.87 \, fs$. For reference, $\epsilon_{BO}^{(1)}$ (red dashed-line) and $\epsilon_{BO}^{(2)}$ (green 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 the $t = 31.87 \, fs$. 
comes identical with a diabatic PES in the direction of the wave-packet motion, (ii) far from the avoided crossing, $\epsilon_{gi}(R,t)$, 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, $\epsilon_{gd}(R,t)$, on the other hand, is piecewise constant in the region where $\epsilon_{gi}(R,t)$ coincides with different BOPESs. Hence $\epsilon_{gd}(R,t)$ has little effect on the gradient of the total TDPES, but may shift the BOPES-pieces of $\epsilon_{gi}(R,t)$ by different constants causing the exact TDPES to be piecewise parallel to the BOPESs. These features of the TDPES support the use of diabatic surfaces as the driving potential when a wave-packet approaches a region of strong NAC. Moreover, they are in agreement with the semi-classical picture of non-adiabatic nuclear dynamics that suggests to calculate the classical forces acting on the nuclei according to the gradient of only one of the BOPESs. We expect that these findings will ultimately lead to improved algorithms for the mixed quantum-classical treatment of electrons and nuclei.

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