Exact Factorization of the Time-Dependent Electron-Nuclear Wave Function

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We present an exact decomposition of the complete wave function for a system of nuclei and electrons evolving in a time-dependent external potential. We derive formally exact equations for the nuclear and electronic wave functions that lead to rigorous definitions of a time-dependent potential energy surface (TDPES) and a time-dependent geometric phase. For the H_2^+ molecular ion exposed to a laser field, the TDPES proves to be a useful interpretive tool to identify different mechanisms of dissociation.

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Treating electron-ion correlations in molecules and solids in the presence of time-dependent external fields is a major challenge, especially beyond the perturbative regime. To make numerical calculations feasible, the description usually involves approximations such as classical dynamics for nuclei with electron-nuclear coupling provided by Ehrenfest dynamics or surface-hopping [1], or even just static nuclei [2]. Quantum features of the nuclear dynamics (e.g., zero-point energies, tunneling, and interference) are included approximately in some methods [3,4], while numerically exact solutions of the time-dependent Schrödinger equation (TDSE) for the coupled system of electrons and nuclei have been given for very small systems like H_2^+ [5]. Clearly, the full electron-nuclear wave function contains the complete information on the system, but it lacks the intuitive picture that potential energy surfaces (PES) can provide. To this end, approximate TDPES were introduced by Kono [6] as instantaneous eigenvalues of the electronic Hamiltonian, and proved extremely useful in interpreting system-field phenomena. The concept of a TDPES arises in a different way in Cederbaum's recent work, where the Born-Oppenheimer (BO) approximation is generalized to the time-dependent case [7].

In the present Letter we provide a rigorous separation of electronic and nuclear motion by introducing an *exact* factorization of the full electron-nuclear wave function. The factorization is a natural extension of the work of Hunter [8], in which an exact decomposition was developed for the static problem. It leads to an exact definition of the TDPES as well as a Berry vector potential. Berry-Pancharatnam phases [9] are usually interpreted as arising from an approximate decoupling of a system from "the rest of the world", thereby making the system Hamiltonian dependent on some "environmental" parameters. For example, in the static BO approximation, the electronic Hamiltonian depends parametrically on the nuclear positions; i.e., the stationary electronic Schrödinger equation is solved for each fixed nuclear configuration $\underline{\underline{\mathbf{R}}}$, yielding $\underline{\underline{\mathbf{R}}}$-dependent eigenvalues (the BO PES) and eigenfunctions (the BO wave functions). If the total molecular wave function is approximated by a single product of a BO wave function and a nuclear wave function, the equation of motion of the latter contains a Berry-type vector potential. One may ask: is the appearance of Berry phases a consequence of the BO approximation or does it survive in the exact treatment? In this Letter we demonstrate that even in the exact treatment of the electron-nuclear system a Berry connection appears and we prove a new relation between this connection and the nuclear velocity field. For a numerically exactly solvable system we calculate the exact TDPES, demonstrate their interpretive power, and compare with approximate treatments. Throughout this Letter we use atomic units and the electronic and nuclear coordinates are collectively denoted by $\underline{\mathbf{r}}$, $\underline{\underline{\mathbf{R}}}$. The Hamiltonian for a system of interacting electrons and nuclei, evolving under a time-dependent external potential, may be written as

$$\hat{H} = \hat{H}_{\mathrm{BO}} + V_{\mathrm{ext}}^{e}(\underline{\mathbf{r}}, t) + \hat{T}_n(\underline{\underline{\mathbf{R}}}) + V_{\mathrm{ext}}^{n}(\underline{\underline{\mathbf{R}}}, t), \tag{1}$$

where $\hat{H}_{\mathrm{BO}}$ is the traditional BO electronic Hamiltonian,

$$\hat{H}_{\mathrm{BO}} = \hat{T}_e(\underline{\mathbf{r}}) + \hat{W}_{ee}(\underline{\mathbf{r}}) + V_{en}(\underline{\mathbf{r}}, \underline{\underline{\mathbf{R}}}) + \hat{W}_{nn}(\underline{\underline{\mathbf{R}}}). \tag{2}$$

Here $\hat{T}_n(\hat{T}_e)$ is the nuclear (electronic) kinetic energy operator, $W_{nn}(W_{ee})$ is the nuclear-nuclear (electron-electron) interaction, and $V_{\mathrm{ext}}^{n}(\underline{\underline{\mathbf{R}}}, t)$ and $V_{\mathrm{ext}}^{e}(\underline{\mathbf{r}}, t)$ are time-dependent external potentials acting on the nuclei and electrons, respectively. The complete electron-nuclear wave function satisfies the TDSE:

$$\hat{H}\Psi(\underline{\mathbf{r}}, \underline{\underline{\mathbf{R}}}, t) = i\partial_t \Psi(\underline{\mathbf{r}}, \underline{\underline{\mathbf{R}}}, t). \tag{3}$$

The central statement of this Letter is the following:

Theorem I.—(a) The *exact* solution of Eq. (3) can be written as a single product

$$\Psi(\underline{\mathbf{r}}, \underline{\underline{\mathbf{R}}}, t) = \Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}}, t)\chi(\underline{\underline{\mathbf{R}}}, t), \tag{4}$$

where $\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}}, t)$ satisfies the normalization condition,

$$\int d\underline{\mathbf{r}} |\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}}, t)|^2 = 1, \tag{5}$$

for any fixed nuclear configuration, $\underline{\underline{\mathbf{R}}}$, at any time t.

(b) The wave functions $\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}}, t)$ and $\chi(\underline{\underline{\mathbf{R}}}, t)$ satisfy

$$(\hat{H}_{\mathrm{el}}(\underline{\mathbf{r}}, \underline{\underline{\mathbf{R}}}, t) - \epsilon(\underline{\underline{\mathbf{R}}}, t))\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}}, t) = i\partial_t \Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}}, t), \tag{6}$$

$$\left(\sum_{\nu=1}^{N_n} \frac{1}{2M_\nu}(-i\nabla_\nu + \mathbf{A}_\nu(\underline{\underline{\mathbf{R}}}, t))^2 + \hat{V}^n_{\mathrm{ext}}(\underline{\underline{\mathbf{R}}}, t) + \epsilon(\underline{\underline{\mathbf{R}}}, t)\right) \times \chi(\underline{\underline{\mathbf{R}}}, t) = i\partial_t \chi(\underline{\underline{\mathbf{R}}}, t), \tag{7}$$

where the electronic Hamiltonian is

$$\hat{H}_{\mathrm{el}}(\underline{\mathbf{r}}, \underline{\underline{\mathbf{R}}}, t) = \hat{H}_{\mathrm{BO}} + V^e_{\mathrm{ext}}(\underline{\mathbf{r}}, t) + \sum_{\nu=1}^{N_n} \frac{1}{M_\nu} \times \left[\frac{(-i\nabla_\nu - \mathbf{A}_\nu(\underline{\underline{\mathbf{R}}}, t))^2}{2} + \left(\frac{-i\nabla_\nu \chi}{\chi} + \mathbf{A}_\nu(\underline{\underline{\mathbf{R}}}, t)\right)(-i\nabla_\nu - \mathbf{A}_\nu(\underline{\underline{\mathbf{R}}}, t))\right]. \tag{8}$$

Here the scalar and vector potential terms are

$$\epsilon(\underline{\underline{\mathbf{R}}}, t) = \langle \Phi_{\underline{\underline{\mathbf{R}}}}(t) | \hat{H}_{\mathrm{el}}(\underline{\mathbf{r}}, \underline{\underline{\mathbf{R}}}, t) - i\partial_t | \Phi_{\underline{\underline{\mathbf{R}}}}(t)\rangle_{\underline{\mathbf{r}}} \tag{9}$$

$$\mathbf{A}_\nu(\underline{\underline{\mathbf{R}}}, t) = \langle \Phi_{\underline{\underline{\mathbf{R}}}}(t) | -i\nabla_\nu \Phi_{\underline{\underline{\mathbf{R}}}}(t)\rangle_{\underline{\mathbf{r}}} \tag{10}$$

where $\langle ..|..|..\rangle_{\underline{\mathbf{r}}}$ denotes an inner product over all electronic variables only.

Proof.—Part (a) We must show that the exact solution $\Psi(\underline{\mathbf{r}}, \underline{\underline{\mathbf{R}}}, t)$ of the full TDSE (3) can be factorized as in Eqs. (4) and (5). To show this, choose at each point in time $\chi(\underline{\underline{\mathbf{R}}}, t) = e^{iS(\underline{\underline{\mathbf{R}}}, t)}\sqrt{\int d\underline{\mathbf{r}} |\Psi(\underline{\mathbf{r}}, \underline{\underline{\mathbf{R}}}, t)|^2}$ and $\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}}, t) = \Psi(\underline{\mathbf{r}}, \underline{\underline{\mathbf{R}}}, t)/\chi(\underline{\underline{\mathbf{R}}}, t)$, where $S(\underline{\underline{\mathbf{R}}}, t)$ is real. The normalization condition (5) then follows immediately.

Part (b) To derive Eqs. (6)–(10), we apply Frenkel's stationary action principle, $\delta \int_{t_0}^{t_1} dt \langle \Psi | \hat{H} - i\partial_t | \Psi \rangle = 0$, to the wave function (4). We require the action to be stationary with respect to variations in $\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}}, t)$ and $\chi(\underline{\underline{\mathbf{R}}}, t)$, subject to the condition (5). This then leads, after some algebra, to Eqs. (6)–(10). Hence, the product wave function Eq. (4) is a stationary point of the action functional, but we still have to prove that this stationary point corresponds to an *exact* solution of the TDSE. By evaluating $i\partial_t(\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}}, t)\chi(\underline{\underline{\mathbf{R}}}, t))$, and inserting Eqs. (6) and (7), we verify that the full TDSE (3) is satisfied.

Theorem II.—(a) Eqs. (6)–(8) are form invariant under the following gaugelike transformation

$$\begin{aligned} \Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}}, t) &\to \tilde{\Phi}_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}}, t) = \exp(i\theta(\underline{\underline{\mathbf{R}}}, t))\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}}, t), \\ \chi(\underline{\underline{\mathbf{R}}}, t) &\to \tilde{\chi}(\underline{\underline{\mathbf{R}}}, t) = \exp(-i\theta(\underline{\underline{\mathbf{R}}}, t))\chi(\underline{\underline{\mathbf{R}}}, t), \end{aligned} \tag{11}$$

$$\begin{aligned} \mathbf{A}_\nu(\underline{\underline{\mathbf{R}}}, t) &\to \tilde{\mathbf{A}}_\nu(\underline{\underline{\mathbf{R}}}, t) = \mathbf{A}_\nu(\underline{\underline{\mathbf{R}}}, t) + \nabla_\nu \theta(\underline{\underline{\mathbf{R}}}, t) \\ \epsilon(\underline{\underline{\mathbf{R}}}, t) &\to \tilde{\epsilon}(\underline{\underline{\mathbf{R}}}, t) = \epsilon(\underline{\underline{\mathbf{R}}}, t) + \partial_t \theta(\underline{\underline{\mathbf{R}}}, t). \end{aligned} \tag{12}$$

(b) The wave functions $\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}}, t)$ and $\chi(\underline{\underline{\mathbf{R}}}, t)$ yielding a given solution, $\Psi(\underline{\mathbf{r}}, \underline{\underline{\mathbf{R}}}, t)$, of Eq. (3) are unique up to within the $(\underline{\underline{\mathbf{R}}}, t)$-dependent phase transformation (11).

Proof.—The form invariance of Eqs. (6)–(8) is easily verified by inserting (11) and (12) into Eqs. (6)–(8) which proves part (a). To prove part (b), assume the exact wave function can be represented by two different products: $\Psi(\underline{\mathbf{r}}, \underline{\underline{\mathbf{R}}}, t) = \Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}}, t)\chi(\underline{\underline{\mathbf{R}}}, t) = \tilde{\Phi}_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}}, t)\tilde{\chi}(\underline{\underline{\mathbf{R}}}, t)$. Defining $g(\underline{\underline{\mathbf{R}}}, t) := \chi(\underline{\underline{\mathbf{R}}}, t)/\tilde{\chi}(\underline{\underline{\mathbf{R}}}, t)$, then $|\tilde{\Phi}_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}}, t)|^2 = |g(\underline{\underline{\mathbf{R}}}, t)|^2 |\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}}, t)|^2$. Integrating this over $\underline{\mathbf{r}}$ and using Eq. (5), we get $|g(\underline{\underline{\mathbf{R}}}, t)|^2 = 1$ implying $g(\underline{\underline{\mathbf{R}}}, t) = e^{i\theta(\underline{\underline{\mathbf{R}}}, t)}$ and hence the desired result $\tilde{\Phi}_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}}, t) = e^{i\theta(\underline{\underline{\mathbf{R}}}, t)}\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}}, t)$.

The wave functions $\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}}, t)$ and $\chi(\underline{\underline{\mathbf{R}}}, t)$ have a clear-cut physical meaning: $|\chi(\underline{\underline{\mathbf{R}}}, t)|^2 = \int |\Psi(\underline{\mathbf{r}}, \underline{\underline{\mathbf{R}}}, t)|^2 d\underline{\mathbf{r}}$ is the probability density of finding the nuclear configuration $\underline{\underline{\mathbf{R}}}$ at time t, and $|\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}}, t)|^2 = |\Psi(\underline{\mathbf{r}}, \underline{\underline{\mathbf{R}}}, t)|^2/|\chi(\underline{\underline{\mathbf{R}}}, t)|^2$ is the conditional probability of finding the electrons at $\underline{\mathbf{r}}$, given that the nuclear configuration is $\underline{\underline{\mathbf{R}}}$. At locations where $|\chi(\underline{\underline{\mathbf{R}}}, t)|^2$ approaches zero the TDPES may show peaks, in close analogy to the "quantum potential" in the Bohmian formulation of quantum mechanics.

Equations (6)–(10) determine the *exact* time-dependent molecular wave function, given an initial state. As written, the nuclear equation is particularly appealing as a Schrödinger equation with both scalar and vector-potential coupling terms contributing effective forces on the nuclei including any geometric phase effects. We call $\epsilon(\underline{\underline{\mathbf{R}}}, t)$ and $\mathbf{A}(\underline{\underline{\mathbf{R}}}, t)$ the exact TDPES and time-dependent Berry connection, respectively. These two quantities mediate the coupling between the nuclear and the electronic degrees of freedom in a formally exact way. Equations (6)–(10) demonstrate that a Berry connection indeed appears in the exact treatment. But does it produce a real effect or can it be gauged away by a suitable choice of $\theta(\underline{\underline{\mathbf{R}}}, t)$ in Eqs. (11) and (12)? To shed some light on this question, we now prove an alternate expression for the vector potential. Inserting $\Phi_{\underline{\underline{\mathbf{R}}}} = \Psi/\chi$ into Eq. (10), and evaluating the nuclear gradient on this quotient, reveals that it is the difference of paramagnetic nuclear velocity fields derived from the full and nuclear wave functions:

$$\mathbf{A}_\nu(\underline{\underline{\mathbf{R}}}, t) = \frac{\mathrm{Im}\langle \Psi(t) | \nabla_\nu \Psi(t)\rangle_{\underline{\mathbf{r}}}}{|\chi(\underline{\underline{\mathbf{R}}}, t)|^2} - \frac{\mathrm{Im}(\chi^* \nabla_\nu \chi)}{|\chi(\underline{\underline{\mathbf{R}}}, t)|^2}. \tag{13}$$

This equation is interesting in several respects. First, writing $\chi(\underline{\underline{\mathbf{R}}}, t) = e^{iS(\underline{\underline{\mathbf{R}}}, t)}|\chi(\underline{\underline{\mathbf{R}}}, t)|$, the last term on the right-hand side of Eq. (13) can be represented as $\nabla_\nu S(\underline{\underline{\mathbf{R}}}, t)$, so it can be gauged away. Consequently, any true Berry connection (that cannot be gauged away) must come from the first term. If the exact $\Psi(t)$ is real-valued (e.g., for a non-current-carrying ground state) then the first term on the right-hand side of Eq. (13) vanishes and hence the exact Berry connection vanishes. Second, since $\mathrm{Im}\langle\Psi(t)|\nabla_\nu\Psi(t)\rangle_{\underline{\underline{\mathbf{r}}}}$ is the true nuclear (many-body) current density, Eq. (13) implies that the gauge-invariant current density, $\mathrm{Im}(\chi^*\nabla_\nu\chi) + |\chi|^2\mathbf{A}_\nu$, that follows from Eq. (7) does indeed reproduce the exact nuclear current density [10]. Hence, the solution $\chi(\underline{\underline{\mathbf{R}}}, t)$ of Eq. (6) is, in every respect, the proper nuclear many-body wave function: Its absolute-value squared gives the exact nuclear (N-body) density while its phase yields the correct nuclear (N-body) current density.

In the following, we first discuss some limiting cases of the exact Eqs. (6)–(10). Fixing the gauge via $\langle\Phi_{\underline{\underline{\mathbf{R}}}}(t)|\partial_t\Phi_{\underline{\underline{\mathbf{R}}}}(t)\rangle_{\underline{\underline{\mathbf{r}}}} \equiv 0$, the electronic equation reads

$$\hat{H}_{\mathrm{el}}(\underline{\underline{\mathbf{r}}}, \underline{\underline{\mathbf{R}}}, t)\phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}}, t) = i\partial_t\phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}}, t), \tag{14}$$

with $\phi_{\underline{\underline{\mathbf{R}}}} = e^{-i\int^t \epsilon(\underline{\underline{\mathbf{R}}}, \tau)d\tau}\Phi_{\underline{\underline{\mathbf{R}}}}$, while the nuclear equation retains its form Eq. (7) with $\epsilon(\underline{\underline{\mathbf{R}}}, t) = \langle\Phi_{\underline{\underline{\mathbf{R}}}}(t)|\hat{H}_{\mathrm{el}}(\underline{\underline{\mathbf{r}}}, \underline{\underline{\mathbf{R}}}, t)|\Phi_{\underline{\underline{\mathbf{R}}}}(t)\rangle_{\underline{\underline{\mathbf{r}}}}$. Note that the electronic Eq. (14) and the nuclear Eq. (7) have to be propagated simultaneously because the Hamiltonian (8) depends $\chi(\underline{\underline{\mathbf{R}}}, t)$. Taking the large-nuclear-mass limit of Eq. (8), the electronic Hamiltonian reduces to $\hat{H}_{\mathrm{el}} \underset{M\to\infty}{\longrightarrow} \hat{H}_{\mathrm{BO}} + \hat{V}^e_{\mathrm{ext}}$; i.e., the dependence of H_{el} on χ drops out and the electronic Eq. (14) depends on the nuclear configuration $\underline{\underline{\mathbf{R}}}$ only parametrically. So, in this limit, Eq. (14) is propagated in time for each fixed nuclear configuration $\underline{\underline{\mathbf{R}}}$ which is precisely Cederbaum's time-dependent generalization of the BO approximation [7]. Hence, the full Eqs. (6)–(10) can be viewed as an "exactification" of the intuitively appealing procedure of [7]. If, furthermore, we treat the nuclei classically, i.e., use the Hamiltonian (7) to generate classical equations of motion for the nuclei, we obtain

$$M\ddot{\underline{\underline{\mathbf{R}}}}_\nu = \mathbf{E}_\nu + \dot{\underline{\underline{\mathbf{R}}}}_\nu \times \mathbf{B}_\nu, \tag{15}$$

where the electric and magnetic "Berry fields" are given by $\mathbf{E}_\nu = \nabla_\nu\epsilon(\underline{\underline{\mathbf{R}}}, t) - \frac{\partial\mathbf{A}_\nu}{\partial t}$ and $\mathbf{B}_\nu = \nabla_\nu \times \mathbf{A}_\nu$. The additional magnetic field was also found, in the appropriate limit in an exact path-integral approach to the coupled dynamics [11], and also in other work [12]. Being strictly equivalent to the TDSE, the electronic and nuclear Eqs. (6) and (7) provide a rigorous starting point suitable for making systematic semiclassical approximations [13,14] beyond the purely classical limit of Eq. (15) .

We now return to the exact formulation to investigate the TDPES for a numerically exactly solvable model: the H_2^+ molecular ion subject to a linearly polarized laser field. By restricting the motion of the nuclei and the electron to the direction of the polarization axis of the laser field, the problem can be modeled with a 1D Hamiltonian featuring "soft-Coulomb" interactions [15]:

$$\hat{H}(t) = -\frac{1}{M}\frac{\partial^2}{\partial R^2} + \frac{1}{\sqrt{0.03 + R^2}} - \frac{1}{2\mu_e}\frac{\partial^2}{\partial z^2} + \hat{V}_l(z, t) - \frac{1}{\sqrt{1 + (z - R/2)^2}} - \frac{1}{\sqrt{1 + (z + R/2)^2}}, \tag{16}$$

where R and z are the internuclear distance and the electronic coordinate as measured from the nuclear center-of-mass, respectively, and the electronic reduced mass is given by $\mu_e = (2M)/(2M + 1)$, M being the proton mass. The laser field represented by $\hat{V}_l(z, t) = q_e z E(t)$, where $E(t)$ denotes the electric field amplitude and the reduced charge $q_e = (2M + 2)/(2M + 1)$. We consider a $\lambda = 228$ nm laser field, represented by $E(t) = E_0 f(t) \times \sin(\omega t)$, for two peak intensities, $I_1 = |E_0|^2 = 10^{14}\ \mathrm{W/cm^2}$ and $I_2 = |E_0|^2 = 2.5 \times 10^{13}\ \mathrm{W/cm^2}$. The envelope function $f(t)$ is chosen such that the field is linearly ramped from zero to its maximum strength at $t =$ 7.6 fs and thereafter held constant.

Starting from the exact ground state as the initial condition, we propagate the TDSE numerically to obtain the full molecular wave function $\Psi(z, R, t)$. As there is only one nuclear degree of freedom (after separating off the center-of-mass motion), we can fix the gauge in Eqs. (11) and (12) such that the vector potential (13) is always zero. From the computed exact time-dependent molecular wave function we compute the TDPES's; these, along with the corresponding nuclear density, $|\chi(R, t)|^2$, are plotted in Fig. 1 at six snapshots of time. The initial TDPES lies practically on top of the ground-state BO surface, which is plotted in all the snapshots for comparison. Figure 2 shows the exact internuclear distance $\langle\Psi(t)|\hat{R}|\Psi(t)\rangle$, along with the results from three approximate methods: (i) the usual Ehrenfest approximation [i.e., Eq. (15)]. (ii) the "exact-Ehrenfest" approximation, which substitutes the exact TDPES for the Ehrenfest potential in the usual Ehrenfest approach and, (iii) an uncorrelated approach, the time-dependent Hartree (self-consistent field) approximation $\Psi_H(\underline{\underline{\mathbf{r}}}, \underline{\underline{\mathbf{R}}}, t) = \phi(\underline{\underline{\mathbf{r}}}, t)\chi(\underline{\underline{\mathbf{R}}}, t)$, i.e., the electronic part does not depend on $\underline{\underline{\mathbf{R}}}$ at all. Figure 2 shows that for the intensity I_1, all methods yield dissociation, while for the weaker I_2, only the exact does. We now discuss how the TDPES contains the signature of this behavior. Note that the laser-field does not couple directly to the nuclear relative coordinate R, but only indirectly via the TDPES.

$I_1 = |E_0|^2 = 10^{14}\ \mathrm{W/cm^2}$: The dissociation of the molecule is dramatically reflected in the exact TDPES, whose well flattens out, causing the nuclear density to spill to larger separations. Importantly, the tail of the TDPES alternately falls sharply and returns in correspondence with the field, letting the density out; the TDPES is the only potential acting on the nuclear system and transfers energy

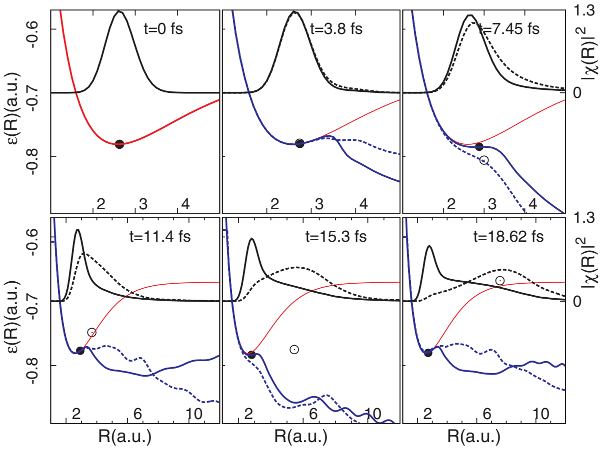

FIG. 1 (color online). Snapshots of the TDPES (blue lines) and nuclear density (black) at times indicated, for the H_2^+ molecule subject to the laser-field (see text), $I_1 = 10^{14}$ W/cm^2 (dashed line) and $I_2 = 2.5 \times 10^{13}$ W/cm^2 (solid line). The circles indicate the position and energy of the classical particle in the exact-Ehrenfest calculation (I_1: open, I_2: solid). For reference, the ground-state BO surface is shown as the thin red line.

from the accelerated electron to the nuclei. The expectation value of the internuclear distance in Fig. 2, demonstrates that among all the approximate calculations employed here, the exact-Ehrenfest is most accurate. Surprisingly, it even does better than TD-Hartree which treats the protons quantum mechanically, thus showing the importance of electron-nuclear correlation.

$I_2 = |E_0|^2 = 2.5 \times 10^{13}$ W/cm^2: From Fig. 2, the exact calculation leads to dissociation, while none of the approximations do, in contrast to the previous case. The TDPES of Fig. 1, suggests that tunneling is the leading mechanism for the dissociation: a well remains at all times that traps a classical particle, which would oscillate inside it, as indeed reflected in Fig. 2. (See also the solid circles in Fig. 1). Although the tail has similar oscillations as for I_1, this does not lead to dissociation of classical nuclei due to the barrier; the TDPES in this case transfers the field energy to the nuclei via tunneling. Although the exact-Ehrenfest has a larger amplitude of oscillation than the others, it ultimately cannot tunnel through the barrier.

This example demonstrates how studying the TDPES reveals the mechanism of dissociation. Because the TDPES includes the electron-nuclear correlation exactly, we believe the exact-Ehrenfest dynamics is the best one could do within a classical treatment of the nuclei. There is a need to go beyond classical dynamics when the dissociation proceeds mainly via tunneling.

In conclusion, we have presented a rigorous factorization of the complete molecular wave function into an electronic contribution, $\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}}, t)$, and a nuclear part, $\chi(\underline{\underline{\mathbf{R}}}, t)$. The exact nuclear N-body density is $|\chi(\underline{\underline{\mathbf{R}}}, t)|^2$ while $|\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}}, t)|^2$ represents the conditional probability of finding the electrons at $\underline{\underline{\mathbf{r}}}$, given the nuclear configuration $\underline{\underline{\mathbf{R}}}$. Their exact equations of motion are deduced. Via these equations, the TDPES (9) and the time-dependent Berry connection (10) are defined as rigorous concepts. We demonstrated with numerical examples that the TDPES is a powerful tool to analyze and interpret different types of dissociation processes (direct vs tunneling). The exact splitting of electronic and nuclear degrees of freedom presented by Eqs. (6)–(10) lends itself as a rigorous starting point for making approximations, especially for the systematic development of semiclassical approximations. As a first step we have shown how the Ehrenfest equations with Berry potential emerge from treating the nuclei classically in the large-nuclear-mass limit.

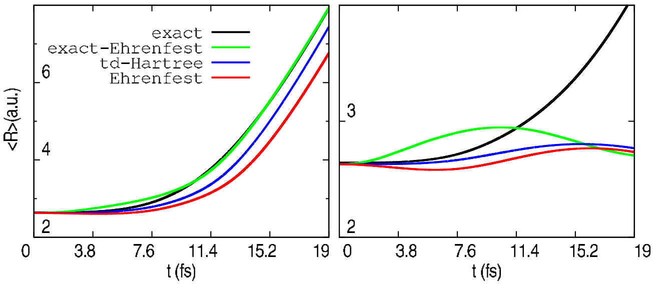

FIG. 2 (color online). The internuclear separation $\langle R \rangle(t)$ for the same intensities as in Fig. 1. Left panel : I_1. Right panel : I_2.

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