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Control of charge migration in molecules by ultrashort laser pulses

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Due to electronic many-body effects, the ionization of a molecule can trigger ultrafast electron dynamics appearing as a migration of the created hole charge throughout the system. Here we propose a scheme to control the charge-migration dynamics with a single ultrashort laser pulse. We demonstrate by fully *ab initio* calculations on a molecule containing a chromophore and amine moieties that simple pulses can be used to stop the charge-migration oscillations and localize the charge on the desired site of the system. We argue that this control may be used to predetermine the follow-up nuclear rearrangement and thus the molecular reactivity.

Since the early days of quantum mechanics, the aim of scientific efforts has been not only to understand the microscopic world, but also to use the quantum properties to control different processes. For example, one may use quantum interference and the properties of the laser-matter interaction in order to exert control over the chemical reactivity of a molecule, a research field known nowadays as "femtochemistry" [1]. In femtochemistry, by specifically tailored femtosecond laser pulses, one tries to steer the motion of the nuclei in the molecule and thus bring the system into the desired reaction channel.

In recent years, the rapid development of attosecond pulse techniques opened the door for studying and eventually controlling electronic motion. As long as the notion of electronic states is valid, the potential-energy landscape in which the nuclei move is formed by the faster moving electrons. It is, therefore, very appealing to use attosecond pulses that modulate the electronic motion such that it triggers some desired nuclear rearrangement. Using the electron dynamics and quantum coherence to induce a particular chemical process is the new paradigm in the emerging field of "attochemistry" (see, e.g., Refs. [2,3]).

This novel concept was to a large extent motivated by the interpretation of the results of a series of pioneering experiments performed by Schlag, Weinkauf, and co-workers (see, e.g., Refs. [4–6]) showing a charge-directed reactivity [7] in electronically excited ionic states of various peptide chains. It was observed that, after localized ionization of the chromophore site of the peptide, the positive charge is transferred to the remote end of the chain, causing a bond breaking. Time-resolved measurement on a smaller, prototype molecule (2-phenylethyl-*N*,*N*-dimethylamine, abbreviated as PENNA) showed that the process takes place on the time scale of few tens of femtoseconds [8,9]. Extensive *ab initio* many-body calculations on PENNA suggested [10] as an explanation that the charge-directed reactivity is concerted electron-nuclear dynamics: Immediately after ionization, pure electron dynamics is triggered and the positive charge starts to oscillate between the chromophore and the remote amine end of the molecule on a few-femtosecond time scale, while at later

times the coupling to the slower nuclear dynamics causes the trapping of the charge on the amine site and the bond breaking.

How is the charge transferred in this pure electronic step? In their pioneering work [11], Cederbaum and Zobeley demonstrated that such a transfer, termed *charge migration*, can be solely driven by many-body effects (electron correlation and electron relaxation). Due to electron correlation, the removal of an electron from a molecular orbital will create an electronic wave packet (a simultaneous population of a multitude of cationic states) which will evolve in time. Charge migration has been intensively studied theoretically [12–16] and has turned out to be a rich phenomenon, with many facets that are rather characteristic of the molecule studied (for a recent review, see Ref. [17]). We note also that, very recently, pure electronic, few-femtosecond charge oscillations were experimentally observed after a broadband ionization of phenylalanine [18] (see also Ref. [19]).

In this Rapid Communication we present a scheme to control the many-body electron dynamics of the charge-migration process by a single ultrashort laser pulse. We show that by appropriately tailored infrared pulses one can stop the pure electronic, few-femtosecond oscillation of the charge, localizing it on the desired site of the molecule 3-methylen-4-penten-*N*,*N*-dimethylamine (MePeNNA), which is a structural analog of the above-mentioned PENNA.

As already noted, the reason for charge migration is that, due to the electronic correlation, the removal of an electron from a particular molecular orbital populates several ionic states, creating in that way an electronic wave packet [11]. Depending on the type of populated cationic states, different mechanisms of charge migration have been identified [12,13,17], with the most common in the outer valence being the so-called hole-mixing mechanism. In hole mixing, two (or more) ionic states appear to be linear combinations of two (or more) one-hole (1h) configurations, representing removal of an electron from a particular molecular orbital.

A showcase example of strong hole mixing appears in the molecule MePeNNA. Our many-body calculations showed that, due to the electron correlation, the ground and the first excited ionic states of the molecule are a strong mixture of two 1h configurations: an electron missing in the highest occupied molecular orbital (HOMO) and an electron missing in the HOMO-1 (see Fig. 1 and Refs. [20,21]). Therefore, if we suddenly remove an electron either from HOMO or from HOMO-1, we will create an electronic wave packet, which

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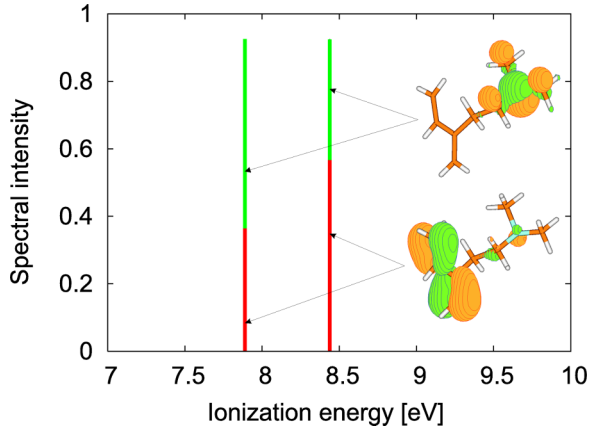†alexander.kuleff@pci.uni-heidelberg.de

FIG. 1. (Color online) Ground and first excited cationic states of the molecule MePeNNA computed using the *ab initio* many-body Green's function ADC(3) method [22]. The next ionic state is located at 10.5 eV. The spectral intensity is defined as the combined weight of the one-hole configurations in the expansion of the ionic state and is a quantity directly related to the ionization cross section [23]. The contributions of the 1h configuration $(HOMO)^{-1}$ are given in red (lower part of the states), while those of $(HOMO-1)^{-1}$ are shown in green (upper part of the states). The two molecular orbitals localized on the chromophore and the amine moieties of the molecule, respectively, are also depicted. The figure is adapted from Ref. [20].

in the Schrödinger representation reads (in atomic units)

$$|\Phi_i(t)\rangle = c_1(t)e^{-iE_It}|I\rangle + c_2(t)e^{-iE_Jt}|J\rangle. \qquad (1)$$

In the above expression, $c_1(t)$ and $c_2(t)$ are the time-dependent (in general, complex) amplitudes of the cationic eigenstates $|I\rangle$ and $|J\rangle$, satisfying $|c_1(t)|^2 + |c_2(t)|^2 = 1$ at all times. Due to the hole-mixing structure of the ionic states, the evolution of the system described by the wave packet (1) will represent an oscillation of the hole charge between the two involved 1h configurations, or between HOMO and HOMO-1. Since HOMO is localized on the chromophore and HOMO-1 on the amine group of the molecule (see Fig. 1), the charge migration will represent an oscillation of the charge between the two ends of the molecule with frequency determined by the energy difference of the two states, $\omega_0 = E_J - E_I$, which is 0.55 eV, meaning that the time needed for the charge to reach the remote end of the molecule is only 3.8 fs [20,21].

Interestingly, the ionization spectrum of MePeNNA suggests that an initial state of the form of Eq. (1) can be achieved experimentally without approaching the sudden-approximation limit of removing an electron from a single orbital. As we see from Fig. 1, to prepare such a wave packet, we need a coherent population of the first two ionic states only, which can be done via a laser pulse with the photon energy centered between the two states and a bandwidth sufficient to embrace both of them. Since the states are about 0.5 eV apart, one needs a pulse with a duration of about 1 fs. The next ionic state is located at 10.5 eV, and therefore its population by such a pulse will be negligible. The initial localization site of the charge (chromophore or N-terminal) is determined by the relative phase between the two ionization channels. The latter can be controlled through the ionization pulse parameters, e.g., by chirping the pulse [24], or by using a π pulse [25].

We now pose the question whether, after the electron dynamics is triggered and the charge starts to bounce back and forth between the two ends of the system, we can control its motion by applying a short laser pulse. The interaction of the system with an external electric field $\vec{E}(t)$ can be described (in the dipole approximation) by the Hamiltonian

$$\hat{H}(t) = \hat{H}_{\text{ion}} - \vec{D} \cdot \vec{E}(t), \qquad (2)$$

where $\hat{H}_{\text{ion}}$ is the full electronic Hamiltonian of the ionized system and $\vec{D} = (\hat{D}_x, \hat{D}_y, \hat{D}_z)$ is the vector operator of the dipole moment. The evolution of the system is governed by the time-dependent Schrödinger equation with the formal solution

$$|\Phi_i(t)\rangle = \mathcal{T} \exp\left(-i \int_0^t \hat{H}(t')dt'\right) |\Phi_i(0)\rangle, \qquad (3)$$

where $\mathcal{T}$ is the so-called time-ordering operator, ensuring that in a Taylor expansion of the exponent the operators are ordered chronologically. In practice, one usually breaks the interval of interest $[0,t]$ into a large number of small increments, or time steps Δt, and Eq. (3) is integrated numerically.

To describe the correlated motion of 69 electrons (the number of electrons in MePeNNA cation) in the presence of a laser field is an extremely difficult problem. To solve it we use *ab initio* methods only. The cationic Hamiltonian $\hat{H}_{\text{ion}}$ is constructed using the so-called non-Dyson algebraic-diagrammatic-construction (ADC) scheme [22] to represent the one-particle Green's function. At the third-order ADC [ADC(3)] level, used in the present calculations, the Hamiltonian is consistent with the exact Green's function up to the third order of perturbation theory with respect to the Hartree-Fock (HF) reference Hamiltonian. Standard double-zeta (DZ) basis sets [26] were used to construct the noncorrelated reference states.

One can include the interaction of the field by diagonalizing the cationic Hamiltonian matrix and using the field-free eigenstates as a basis to expand the dipole operator, computing the transition dipole matrix elements. Alternatively, when the diagonalization is very expensive, one can represent the dipole operator $\vec{D}$ in the many-electron basis of the molecular Hamiltonian (in the present case this is the so-called intermediate-state-representation basis [27]) and then directly propagate with the full Hamiltonian [28]. For this purpose, or to perform the wave-packet propagation, Eq. (3), we used the short-iterative Lanczos technique [29]. Details of this technique, which allow one to study the correlated-electron dynamics in systems containing a few tens of electrons, are given in Ref. [28].

Our aim is to find laser fields $\vec{E}(t)$ which can steer the evolution of the wave function of a system. As mentioned above, under certain ionization conditions, the initial state of the MePeNNA molecule will be a linear combination of the two lowest eigenstates of the ionic Hamiltonian and, therefore, can be regarded as a two-level system. There are numerous protocols suggested in the literature for controlling the quantum dynamics in two-level systems (see, e.g., Refs. [30–33]). Most of these protocols, however, are designed to perform a population inversion, that is, to invert the population distribution between the two states. This is insufficient for our purposes, as we would like to have the freedom to choose

the desired final distribution of the populations starting from any initial one.

Very recently, we proposed a general approach to obtain resonant laser pulses that can drive the populations of a two-level system in a predefined way [34]. If we want the evolution of the system to follow a particular quantum path, that is, that one of the populations in Eq. (1) evolves according to some control function $f(t)$, i.e., $|c_1(t)|^2 = f(t)$, then the field which can drive this transition takes the form [34]

$$E(t) = \frac{1}{\mu} \frac{\dot{f}(t)}{\sqrt{f(t)[1 - f(t)]}} \sin(\omega_0 t + \varphi), \qquad (4)$$

where μ is the projection of the dipole moment on the electric field polarization axis, and φ is the relative phase between the initial amplitudes, $c_1(0)$ and $c_2(0)$, of the populated ionic states. A convenient choice for the control function is [34]

$$f(t) = a_i \left(1 - \frac{1}{1 + e^{-\alpha t}}\right) + a_f \frac{1}{1 + e^{-\alpha t}}, \qquad (5)$$

where a_i and a_f are the initial and the final (target) populations, respectively, of one of the states and the parameter α connects the transition time with the intensity of the field.

It should be noted that the two-level model is used here only to obtain the field parameters. To compute the evolution of the hole charge in MePeNNA molecule in the presence of the control pulse, the propagation was performed with the full Hamiltonian, Eq. (2), as described above.

A convenient quantity for visualization, or to trace the charge dynamics in time and space, is the so-called hole density [11,12]. The hole density is defined as the difference between the electronic density of the neutral and that of the cation

$$Q(\vec{r}, t) = \langle \Psi_0 | \hat{\rho}(\vec{r}) | \Psi_0 \rangle - \langle \Phi_i(t) | \hat{\rho}(\vec{r}) | \Phi_i(t) \rangle, \qquad (6)$$

where $\hat{\rho}(\vec{r})$ is the one-body electronic density operator, $|\Psi_0\rangle$ is the ground state of the neutral, and $|\Phi_i(t)\rangle$ is the propagated cationic wave packet. The quantity $Q(\vec{r}, t)$ describes the density of the hole at position $\vec{r}$ and time t and by construction is normalized at all times t.

Let us now examine two situations of particular interest for achieving control over the charge-migration dynamics, namely, stopping the charge oscillations and localizing the charge on one of the two molecular sites. To be specific, we will assume that the initial ionization of our test molecule, MePeNNA, is performed such that the electron is removed from the HOMO, i.e., the initial hole charge is localized on the chromophore. As discussed above, this will trigger pure electron dynamics in which the charge will oscillate between the chromophore and the amine site, and we would like to apply a control pulse which will stop this oscillation and localize the charge on the amine group or on the chromophore.

Such control can be achieved by a laser pulse obtained via Eqs. (4) and (5) by choosing the desired initial and final populations of the two states in the wave packet. In the case of MePeNNA, if we want to drive the system to a stationary state in which the charge is entirely localized in the HOMO, we need to choose $a_f = 1$, while if we want to localize the charge on the amine site, we need to take $a_f = 0$. The initial population is $a_i = 0.4$, reflecting the fact that an initial state with a hole localized in the HOMO has the form $|\Phi_i(0)\rangle = \sqrt{0.4}|I\rangle + \sqrt{0.6}|J\rangle$ (see also Fig. 1).
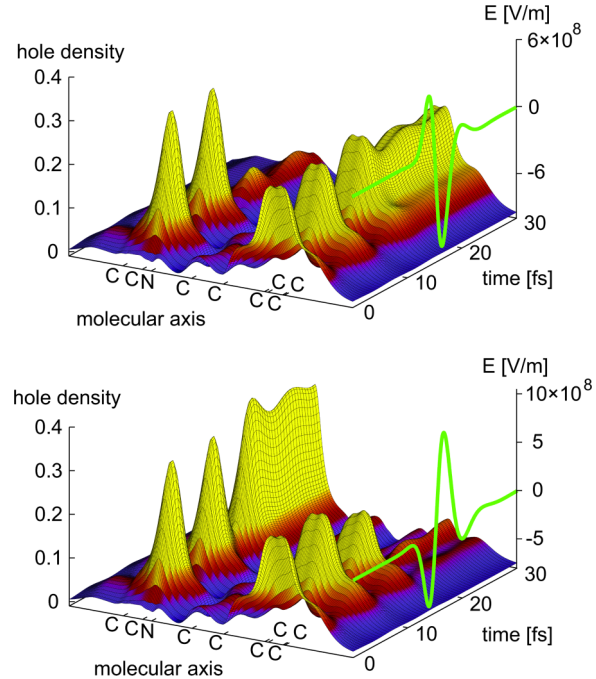

FIG. 2. (Color online) Time evolution of the hole density, Eq. (6), along the molecular axis of the molecule MePeNNA, after an initial localized ionization of the chromophore, controlled with a laser pulse (shown on the right) centered at 15 fs. The molecular axis is chosen to pass through the longest spatial extension of the molecule. Upper panel: The laser pulse is designed to achieve localization of the charge on the chromophore. Lower panel: The laser pulse is designed to achieve localization of the charge on the amine site.

As mentioned above, the parameter α in Eq. (5) controls the interplay between the duration and the intensity of the pulse needed to perform the transition—a slow transition can be achieved with a weak pulse, while a shorter pulse will naturally need higher intensity. Since we want to modulate the charge migration before the nuclear motion will start to influence the dynamics, we would like to use as short a pulse as possible. On the other hand, the high intensity of the control pulse may lead to undesired multiphoton processes, which can, for example, further ionize the system. Therefore, we need to balance between these two factors. In the case of MePeNNA, the minimum pulse duration (corresponding to a single-cycle pulse) needed to perform the transition is about 10 fs, giving an electric field strength which never exceeds 10^9 V/m. This corresponds to a pulse with a peak intensity of about 10^{11} W/cm^2, which is rather weak.

The results of our full propagation, accounting for the influence of the control field with the above parameters, are shown in Fig. 2. The figure depicts the hole density, defined in Eq. (6), of the molecule MePeNNA after creating the initial hole on the chromophore at time $t = 0$ and applying a control laser pulse (also shown in the figure) with the maximum of the field centered at $t = 15$ fs. Immediately after ionization, the charge-migration dynamics takes place with the hole jumping from one end of the system to the other. We clearly see that between $t \sim 10$ and 20 fs, the time during which the system is exposed to the control pulse, the charge oscillations are nearly completely stopped and the hole becomes localized

on the desired site—on the chromophore (upper panel of Fig. 2) or on the amine group (lower panel of Fig. 2). We would also like to emphasize that the charge stays put at the desired site of the molecule *after* the pulse is over, that is, the pulse is tailored such that it brings the system to a superposition of electronic states in which the density is essentially stationary. The small oscillations taking place after the pulse is over reflect the fact that the molecule is, of course, not a perfect two-level system. Because of the electron correlation, in addition to the two mixed 1h configurations, the two involved ionic eigenstates also contain small contributions from the two-hole–one-particle (2h1p) configurations [23]. The latter represent an excitation of an additional electron accompanying the ionized one. The combined weight of the 2h1p configurations forms the missing to one part in the states depicted in Fig. 1. Through the 2h1p configurations, other molecular orbitals also contribute to the dynamics and get populated, while the pulse is optimized to account only for the HOMO and the HOMO-1. Nevertheless, the suggested simple scheme to obtain the needed control-pulse parameters works remarkably well in such a complicated system as the MePeNNA molecule. We note also that the control pulse has a rather simple form and can be synthesized using spatial-light-modulator (e.g., liquid-crystal mask) techniques [35,36].

Let us now comment on a possible further evolution of the studied system. Due to its similarity with the above-mentioned PENNA molecule, one may expect a similar charge-directed reactivity after localized ionization of the chromophore. The charge starts to oscillate between the two ends of the molecule until the nuclear motion eventually traps it at the amine site and the molecule dissociates by breaking the bridging carbon-carbon bond. However, as we have noted above, the nuclear motion is strongly influenced by the electron dynamics and, therefore, by controlling the charge migration we may be able to predetermine the nuclear rearrangement. Localizing the charge on the chromophore may substantially slow down or even prevent the dissociation, while its localization on the amine site will most probably speed up the breakup of the molecule.

To check this plausible hypothesis, one needs a full quantum treatment of the coupled electron-nuclear dynamics. Unfortunately, this is currently out of reach for such large systems. We would like to note, however, that a semiclassical method that might give some hints about how the nuclear motion will be affected by the electron dynamics was recently proposed [37–39] and could be a good starting point for such studies.

Before concluding, we would like to emphasize that the scheme presented in this work is general and not restricted to only stopping the charge-migration oscillations. Through the control function $f(t)$ in Eq. (4), one is able to obtain the pulse shape needed to drive the system to any combination of the two electronic states, and thus bring the ion to the optimum initial condition for the desired follow-up nuclear motion.

We hope that our study will stimulate further theoretical and experimental work on the possibilities to control chemical reactions via the manipulation of the electron dynamics.

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