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Nonlinear dynamics of attosecond charge migration in model carbon chains

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We investigate attosecond charge migration (CM) in model carbon chains by employing tools from nonlinear dynamics. We show that mean-field interactions drive synchronization of the electron motion and give rise to a variety of CM dynamics. Notably, we find that a molecule can support several current-like CM modes, depending on the initial conditions, with periods varying by several hundred attoseconds. We also show that functionalization and hybridization can play an important role in synchronizing CM dynamics. Our results pave the way to understanding the mechanisms that regulates CM dynamics in complex molecules using nonlinear collective effects.

Electron and hole motions in matter are central to physical and chemical processes. For instance, they can induce chemical reactions, photosynthesis and photovoltaics, and charge transfer [1, 2]. At the natural length and time scales of electron motion in molecules – the Angstrom and the attosecond – these coherent ultrafast dynamics are often called charge migration (CM) [3–8]. In this context, CM is understood as the purely-electronic-driven dynamics that unfolds before nuclei have time to move. It can be the precursor for many of the down-stream processes mentioned above [2, 9–11], and therefore a means of understanding and ultimately steering them. The study of molecular CM is currently an active field of research [12–15], however, it is a formidable endeavor. Experimentally it requires the development of multi-dimensional coherent probes with attosecond resolution [2]. Theoretically, it necessitates models with multiple interacting electrons, even when nuclear motion is ignored.

Systematic studies of the mechanisms underlying, and responsible for regulating, CM can appear beyond reach since they involve the analysis of systems with a large number of coupled degrees of freedom. One approach to such large-scale problems is provided by nonlinear dynamics, which has developed general-purpose methods for tackling and understanding the structure of high-dimensional phase spaces. For instance, nonlinear dynamical analyses have been instrumental in many areas of atomic, molecular and optical science, including understanding the bunching mechanism responsible for lasing in free-electron lasers [16], in transition-state theory of chemical reactions [17–19], and for strong-field physics [20–23].

In this Letter, we study the field-free dynamics of a localized hole suddenly introduced into a one-dimensional carbon chain, as a paradigm for CM following ionization. Figure 1 introduces an example of CM within our model. Strikingly, the foreground colormap in the figure reveals a nearly smooth, current-like migration of the hole, which

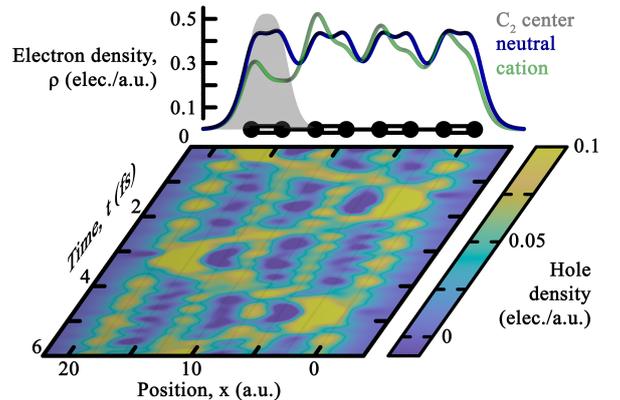


FIG. 1: (color online) Charge-migration dynamics in $(C_2)_4$ following a sudden ionization perturbation localized on the left end of the chain. The graphs at the top show the electron densities of the end C_2 center alone, in the neutral ground state, and in the cation immediately after the ionization perturbation. The foreground colormap corresponds to the subsequent electron-hole-density dynamics, defined as the difference between the neutral ground-state and time-dependent cation densities.

moves through the entire chain in about 1.7 fs. The apparent sustained coherence of a particle-like hole, which remains localized both in space and time, naturally raises the questions: (i) How common is this? (ii) Are there other types of coherent dynamics? If so, what are they? (iii) What are the physical mechanisms that organize and regulate those CM motions? In what follows, we answer these questions by employing tools from nonlinear dynamics. In doing so, we highlight the central role of *dynamical* electron-coupling and synchronization as the engine for CM dynamics in our models, as an alternative to, *e.g.*, few-orbital beating mechanisms that have previously been employed [6, 9, 12]. We also demonstrate the importance of functionalization and hybridization in synchronizing the dynamics, which would open the way for chemically controlling CM in the future.

We focus on generic mechanisms that regulate CM in molecules with multiple interacting electrons. To do so, we consider dimensionally- and functionally-reduced models that reproduce the key elements of the coupled dynamics. More specifically, we systematically consider one-dimensional carbon chains, denoted $(C_2)_n$, with n the number of pairs of ‘‘C’’ centers. These chains are the one-dimensional chemical analogs to three-dimensional alkenes, without the hydrogen centers. We functionalize the chain by adding an electron-heavy ‘‘X’’ center at one end of the molecule, meant to emulate a halogen group. Building on previous successes of time-dependent density-functional theory (TDDFT) in modeling CM in various molecules [12, 13], we likewise consider a mean-field approach. Specifically, we use an average-density self-interaction corrected [24] time-dependent Hartree potential, *i.e.*, TDDFT without an exchange or correlation potential. This allows us to unambiguously determine the role of dynamical mean-field interactions in CM. We describe the electronic structure and dynamics with an orthonormal family of non-interacting one-electron Kohn-Sham (KS) orbitals $\{\phi_k(x; t)\}_k$ [25] such that, in atomic units,

$$i\partial_t\phi_k = \hat{H}_{\text{eff}}[\rho]\phi_k \quad \text{with} \quad \rho = \sum_{k \geq 1} n_k |\phi_k|^2 \quad (1)$$

where the one-body electron density ρ is an explicit nonlinear variable in the mean-field Hamiltonian \hat{H}_{eff} . Here $0 \leq n_k \leq 2$ is the number of electrons in each spin-restricted KS channel. Numerically, we spatially discretize the KS orbitals on a Cartesian grid. For CM-dynamics computations, we propagate the KS Eq. (1) in a basis of molecular orbitals of the corresponding singly-ionized cation using a Crank-Nicholson scheme. We have checked that nearly identical results are obtained by directly integrating Eq. (1) on the grid with a split-operator method. Further details about the X- $(C_2)_n$ molecules’ parameters and the mean-field model can be found in the supplemental material section I [26].

We begin by studying the CM dynamics in a $(C_2)_n$ chain. The bare chain, without functionalization, is highly symmetric and therefore an impractical system for generating a localized ionization-hole in a realistic experimental scenario. However, since the chain is the backbone for the migration dynamics we will consider, it is appropriate to study its dynamics first. Below we will discuss the effects of adding an X center to one end of the chain, as a handle for introducing a localized ionization hole or for steering the CM dynamics.

In Fig. 1 we show an example of CM dynamics in $(C_2)_4$. We create the initial ionization perturbation by suddenly removing a full electron localized on the left end of the chain – see the curves at the top of Fig. 1. As mentioned above, the subsequent field-free evolution, shown on the foreground colormap, reveals an alternating current-like

motion of the hole with a 1.7-fs half period. We have observed similar current-like migration motions when varying the length of the chain (not shown), demonstrating its robustness across the $(C_2)_n$ family. We model ionization from the highest-occupied KS channel, in which we construct the initial localized hole with a linear combination of a few occupied and unoccupied orbitals of the corresponding cation. Note that this linear combination solely reflects the spatial configuration of the electron density right after ionization and does not infer any orbital-beating process in the subsequent dynamics. Additional details about the method we use to create the initially localized hole and how we integrate the subsequent dynamics of Eq. (1) can be found in the supplemental material section II [26].

Aside from the computational cost of integrating the mean-field system of Eqs. (1), one of the main obstacles to systematic studies of CM in molecules is the very large dimension of phase space associated with the many active electrons in the target. These analyses are further complicated by the structure of the TDDFT formalism: The KS-orbitals *dynamical* variables $\{\phi_k\}_k$ represent fictitious electrons interacting via the mean field. As such, they hold very limited physical or chemical meaning for dynamics far from equilibrium, including CM (see discussion below). The *physical* one-body density ρ , on the other hand, hides the organization of the dynamics by incoherently adding the KS-orbital contributions. In the following, we reveal this organization using frequency map analysis (FMA) and explain the mechanisms that regulate coupled multi-electron motions like the alternating current-like migration of Fig. 1.

Generally speaking, FMA follows the main frequency components associated with a dynamical process as a function of a continuously-varied initial condition [27, 28]. In doing so, it can discriminate chaotic regions of phase space – with strong sensitivity to the initial condition – from regular ones. We show an example of FMA for $(C_2)_4$ in Fig. 2. Here we continuously vary the degree of localization of the initial one-electron-hole labeled by ε on Fig. 2: $\varepsilon = 0$ corresponds to the delocalized ground state of the cation while $\varepsilon = 1$ corresponds to the initial hole being fully localized on one end of the chain (similar to the top curves of Fig. 1). In order to highlight migration motions through the entire chain, the complex-valued signal we use in the FMA tracks the time-dependent electron density around one or the other end of the molecule in its real or imaginary part. Further details about the FMA and its implementation can be found in the supplemental material section III [26].

In the region of phase space around the ground state of the cation, roughly $0 \leq \varepsilon \lesssim 0.2$ on the FMA of Fig. 2, we observe frequency components with no or very weak intensity. This is expected given that, by construction, the ground-state electronic configuration leads to a density that does *not* evolve in time in Eq. (1). In the interme-

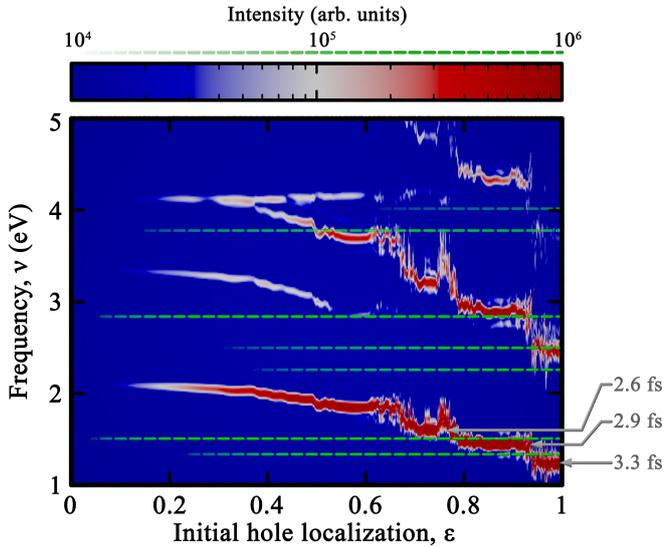


FIG. 2: (color online) Frequency-map analysis of the charge-migration dynamic in $(C_2)_4$. The horizontal axis labels the degree of localization for the initial ionization perturbation: $\varepsilon = 0$ corresponds to the ground state of the cation while $\varepsilon = 1$ is associated with a fully localized hole on one end of the chain. The frequency colormap is obtained with a windowed-Fourier transform, with 100-fs total duration, of a signal tracking migration motions through the entire chain (see text). Dashed horizontal lines label the frequency components in the linear approximation $\hat{\mathcal{H}}_{\text{eff}}[\rho(t)] \approx \hat{\mathcal{H}}_{\text{eff}}[\rho_{\varepsilon=0}]$ in Eq. (1), with the transparency encoding the intensity of those frequency lines.

diagnose region $0.2 \lesssim \varepsilon \lesssim 0.7$ of the map we observe several frequency curves evolving from 2.1 eV and 3.3 eV, respectively, where the ratio of their frequencies is irrational (the frequency curve evolving from 4.2 eV is a harmonic of the 2.1 eV one). These are associated with aperiodic CM dynamics, as discussed below. Finally, for $0.7 \lesssim \varepsilon \leq 1$, we observe a succession of plateaus, between 1 and 1.7 eV for their lowest-frequency component – also labeled with their corresponding periods on the right margin of Fig. 2. This stair-like structure is duplicated at integer multiples of this lowest frequency. Such a frequency composition, with a unique fundamental component plus its harmonics, is consistent with quasi-periodic migration of electron densities through the molecule. Indeed, each of these plateaus is associated with a current-like migration of charge similar to the one displayed in Fig. 1 ($\varepsilon = 0.95$).

The plateau structures observed in the higher part of the FMA of Fig. 2 are significant for several key aspects of CM studies: (i) *dynamical stability* – plateaus like these are signatures of stable regions of phase space, like the islands surrounding elliptic periodic orbits [27]. In turn, this explains the sustained particle-like hole migration observed in Fig. 1 and discussed above. (ii) *parametric stability* – within each plateau of the FMA of Fig. 2, irrespective of the details for the initial ionization perturba-

tion, all current-like motions have the same period. This is essential for experimental applications as it provides a robustness of the migration dynamics against uncertainties in the way the hole might be created. (iii) *multiple migration modes* – the multiplicity of plateaus shows that the same molecule can support several modes of alternating current-like migration, each with a different period varying with as much as 700 as in the FMA of Fig. 2 – see right margin. When varying the length of the chain, we systematically observe similar multiple plateaus, each associated with a current-like CM, therefore demonstrating their robustness across the $(C_2)_n$ family.

As a first attempt to identify the mechanisms responsible for the migration dynamics in $(C_2)_n$ chains, we consider a linearization of the mean-field Hamiltonian of Eq. (1) by fixing $\hat{\mathcal{H}}_{\text{eff}}[\rho(t)] \approx \hat{\mathcal{H}}_{\text{eff}}[\rho_{\varepsilon=0}]$, with $\rho_{\varepsilon=0}$ the time-independent ground-state density of the cation. The linearization reduces the KS-orbital dynamics to the beating between the ground-state molecular orbitals of the cation. In Fig. 2, we plot the frequency components of the FMA, for the linear approximation, with dashed horizontal lines. While, at first glance, the plateaus in the FMA of the full time-dependent mean-field system (colormap) seem to gravitate around some of the linear-approximation frequencies, a closer comparison between the two reveals qualitatively different dynamical structures: over the entire range of phase space we investigate, nowhere does the linear approximation manage to accurately predict the electron/hole dynamics. Instead, we have found that the orbital-beating picture associated with the linear approximation is only valid in the neighborhood of the ground state of the cation, where there is barely any electron dynamics – see supplemental material section III. B [26]. Our analysis therefore highlights the central role played by time-dependent mean-field correlations between electrons in regulating the observed CM, since these correlations are removed in the linear approximation, which differs essentially from the full analysis.

Globally, the FMA of Fig. 2 shows that, in the part of phase space we investigate here, the density dynamics associated with Eq. (1) has at most a handful of well-defined contributing fundamental frequencies. This fully correlated dynamics also has noticeably fewer frequency components than its linear approximation (compare dashed horizontal lines and the colormap), which seems consistent with observations in full-dimensional simulations performed in various organic molecules [6, 12]. Both findings are rather unexpected for a dynamical system with many coupled degrees of freedom. Instead, our analysis suggests that CM motions in $(C_2)_n$ are regulated by synchronization-type dynamics. Here, synchronization refers to the self-organization and coalescence of several degrees of freedom around an effective dynamics in reduced dimension [29]. Synchronization phenomena have been identified throughout physics, engineering and biology [30–32].

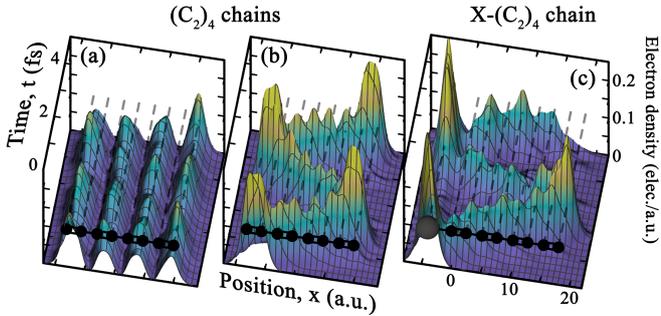


FIG. 3: (color online) Evolution of the contribution to the total electron density from the ionized KS channel. Panels (a,b) correspond to the $(C_2)_4$ -chain model, with initial ionization localization $\varepsilon = 0.2$ and $\varepsilon = 0.95$, respectively. Panel (c) corresponds to the functionalized $X-(C_2)_4$ system. Details about the molecular models and parameters can be found in the supplemental material section I. B [26].

The synchronized CM dynamics is most clearly apparent in the contribution to the total electron density from the ionized KS channel. To illustrate this, in Fig. 3 (a), we show the density in the intermediate part of phase-space, with $\varepsilon = 0.2$. Because of the two irrational fundamental frequency components in the dynamics – see discussion above – the density exhibits a succession of oscillations around each C_2 center, with no apparent global period or pattern. Accordingly, we observe a similar aperiodic dynamics in the hole density (not shown). Looking back at Fig. 2, we see that these two fundamental frequencies $\nu_1 \approx 2.1$ eV and $\nu_2 \approx 3.3$ eV shift in energy with increasing localization of the initial ionization perturbation (increasing ε). This shift is driven by the nonlinear electronic coupling in Eq. (1). Eventually, around $\varepsilon \approx 0.7$, the higher fundamental frequency merges with the first harmonic of the other component $\nu_2 = 2 \times \nu_1 \approx 3.2$ eV. As a result, the overall electron-density dynamics gets locked in a global quasi-periodic motion, which leads to the current-type migration motions discussed above. This locked dynamics is clearly visible in Fig. 3 (b), where the density in the ionized KS channel remains localized both in space and time while it migrates through the chain.

Comparing Fig. 3 (b) and Fig. 1, we see that the synchronized particle-like density in the ionized KS channel follows the migration of the total hole density in the target. This similarity is not accidental and stems from (i) the synchronized one-electron KS orbital associated with the ionized channel, and (ii) the orthogonality requirement for the other fully occupied KS channels. More broadly, this suggests that, while they cannot be measured experimentally, looking at partial contributions from ionized/perturbed KS orbitals can be illuminating for theoretical CM studies.

As discussed above, the experimental relevance of the $(C_2)_4$ chain on its own is limited by the impracticality

of inducing a localized hole at one end of a symmetric target. To circumvent this issue, we can break the chain symmetry by attaching a suitable functional group at one end of the chain, and leverage this to generate the initially-localized electron-hole, for instance using strong-field ionization [7]. To model functionalization, we add an electron-heavy “X” atomic center to the $(C_2)_n$ chain, meant to emulate a halogen – see supplemental material section I. B [26] for details about the $X-(C_2)_4$ model and parameters.

In Fig. 3 (c), we show a successful example of $X-(C_2)_4$ functionalization where the X center is used to create the initial localized electron perturbation in the ionized KS channel, which then migrates back and forth through the entire molecule. Here as well, we have confirmed that the total hole density in the molecule follows the same current-like motion as that of the density in that KS channel. Importantly, with varying the parameters of the X center, *e.g.*, as would be obtained by using different functional groups, we have found that not all manage to transmit their initial X-localized hole in to the chain, as in Fig. 3 (c). For that to happen, the X-atomic and $(C_2)_4$ -molecular orbitals need to hybridize in forming the $X-(C_2)_4$ compound. Intuitively, such delocalized hybridized orbitals provide a bridge for the electron density to move between the two parts of the molecule.

Through the phase-space analysis of $X-(C_2)_n$ systems, we have identified an additional potential use of functionalization for controlling CM. Specifically, we compared the dynamics when starting the localized ionization-perturbation on the chain side of the molecule and using various X effective potentials. Even when the migration remains confined to the $(C_2)_n$ part of the molecule, the attached X function can alter the properties of the chain, including its ability to support current-like migrations. We provide an example of this point by comparing FMA and sample CM dynamics in the supplemental material Fig. S3 [26]. Clearly, this demonstrates the potential for chemically tailoring CM in molecules.

In conclusion, using nonlinear dynamical tools, we have performed systematic analyses of charge migration in carbon-chain-like molecules. Our analyses reveal that the same molecule can support several types of ultrafast electron motions, including regular aperiodic and quasi-periodic dynamics, each identified with their characteristic signatures in their frequency maps. Driven by nonlinear coupling between the time-dependent multiple interacting electrons, we have identified apparent synchronization-like mechanisms that ultimately lead to current-like CM modes in the molecule. Notably, qualitatively similar current-like modes with periods varying by several hundred attoseconds can be found in the same compound. Finally, we have shown the potential for chemical control of migration motions with molecular functionalization, both in creating the initially localized electron hole and for its subsequent time evolution.

In this Letter, we elected for simplified molecular models to demonstrate our analysis tools and highlight the mechanisms that regulate CM motions in them. Critically, these emerge as a result of the dynamical mean-field interaction alone. It suggests that synchronization effects are sufficient to organize the electrons into CM modes, even without explicit exchange or correlation interactions. While it would likely alter their period and synchronization condition, we expect these mechanisms to subsist when adding exchange-correlation interactions. Moreover, this synchronization gives stability to the CM improving the likelihood that these will be the modes that can be realized in real systems and observed in experiments. The results presented in this paper, along with the analysis tools that we employed, can help provide important perspectives for the design of future CM studies.

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