Quantum Control of Electron Wavepacket Dynamics in Molecules by Trains of Half-Cycle Pulses

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Abstract. We investigate localization dynamics of electrons in small molecular model systems driven by optimally shaped trains of half-cycle pulses (HCP). We explore the parameter space defining these HCP trains and demonstrate that the timing and strength of the first HCP “kicks” define the efficiency and direction of electron localization. As an extension, we also demonstrate that electron localization can be achieved in simple four-atomic linear molecules opening the route towards selective charge transport along chains of atoms.

1. Introduction
The possibility to monitor ultrafast dynamics on the femtosecond timescale, the timescale of nuclear motion [1], evoked the desire not only to observe but to actively control nuclear dynamics [2–7]. With the advent of attosecond physics, it has become possible to extend this approach to electronic dynamics [8], inspiring likewise attempts to actively control electronic dynamics. Control requires either ultrashort (attosecond) pulses (with spectra extending to the EUV domain) or intense (infrared) fields facing the additional challenge of complicated strong-field dynamics.

Recently, quantum control protocols steering the dynamics of ionized electrons by either two-color laser fields [9] or elliptically polarized single-color fields [10,11] were suggested. It has been demonstrated that bound electrons can be steered in real time by either carrier-envelope phase control of few-cycle infrared laser pulses [12–18] or by control over delay time between two laser pulses [19,20]. Alternatively, phase- and amplitude-shaped electric fields may steer electronic and coupled nuclear-electronic dynamics [21]. We have recently demonstrated that breaking the inversion symmetry of the electric field relative to the polarization axis by e.g. mixing even and odd harmonic colours of the fundamental frequency opens new possibilities to steer electronic dynamics on the femto- and sub-femtosecond time-scale [17,22]. By the combination of several harmonic orders with locked phases, a train of unidirectional half-cycle laser pulses (HCP) can be formed.

In this work, we present numerical results demonstrating efficient control of electron localization dynamics in small molecular systems by trains of HCPs. While for dissociating systems the electronic motion “freezes out” upon dissociation, for systems with bound states localization is only transient for homonuclear diatomic molecules. We also present results for a
four-atomic system of reduced dimensionality to demonstrate that the quantum control protocol can be extended towards longer, chain-like molecules.

The paper is organized as follows: Section 2 briefly describes the model systems representing different molecules. In Section 3, the numerical results for quantum control of electronic localization dynamics in bound systems are presented, together with a description of the underlying physical mechanism. Finally, Section 4 contains a brief summary and conclusions.

2. Brief description of the theoretical methods

2.1. Model systems describing bound molecular ions

We consider the coupled nuclear-electronic dynamics of prototype molecular systems representing simple diatomic and four-atomic molecular ions. The model potentials are described by one-dimensional soft-core potentials with a smoothing function $\alpha(R)$ depending on the nuclear degree of freedom $R$. These potentials are parameterized such that the two lowest lying electronic states of the model system are bound states with even and odd symmetry. The Hamiltonian of these systems with one electronic degree of freedom ($-\infty < x < \infty$) and one nuclear degree of freedom ($0 \leq R < \infty$) is given by the sum of kinetic ($T$) and potential terms ($V$) and the interaction with the external field $E(t)$ (atomic units are used if not stated otherwise):

$$H = T_x + T_R + V(x, R) + x E(t).$$  (1)

The potential term has a soft-core form with a smoothing function $\alpha(R)$, which enables control over the equilibrium internuclear distance, the energy gap between the electronic states, and the ionisation potential. The particular choice of their shape will be given below. Being interested in linearly-polarized fields and dynamics developing mainly along the molecular axis, the relevant features can be extracted from a one-dimensional description. We believe that a full three-dimensional calculation might yield different absolute values for the observables of interest, here the absolute asymmetry, but would not fundamentally alter the underlying mechanisms.

The time-dependent Schrödinger equation (TDSE) for the coupled electronic and nuclear coordinate is

$$i \frac{\partial}{\partial t} \Psi(x, R, t) = \hat{H} \Psi(x, R, t),$$  (2)

with the initial condition

$$\Psi(x, R, t = 0) = \varphi_g(x; R) \chi_0(R).$$  (3)

In eq. 3, $\varphi_g(x; R)$ is the electronic ground state with gerade symmetry, and $\chi_0(R)$ the vibrational ground state. The calculations are performed on a 2-dimensional grid, using the split-operator technique [23] with a total number of 512 points in $R$ and 1024 in $x$. The grid in $R$ is defined from 0.1 to 32 a.u., and the grid in $x$ from $-100$ to $100$ a.u.

Additionally, we have performed calculations within the basis expansion of 2 Born-Oppenheimer (BO) states with the nuclear Schrödinger equation

$$i \frac{\partial}{\partial t} \begin{pmatrix} \chi_g(R, t) \\ \chi_u(R, t) \end{pmatrix} = \begin{pmatrix} \frac{1}{2M} \frac{\partial^2}{\partial R^2} I + \begin{pmatrix} V_g(R) & -\mu_{gu}(R) E(t) \\ -\mu_{gu}(R) E(t) & V_u(R) \end{pmatrix} \end{pmatrix} \begin{pmatrix} \chi_g(R, t) \\ \chi_u(R, t) \end{pmatrix}. $$  (4)

In above equation, $M$ is the reduced nuclear mass, $I$ is the unit matrix, and $\mu_{gu}(R)$ is the transition dipole between electronic states $g$ and $u$. The potential curves $V_i(R)$ are the electronic eigenenergies, parametrically depending on $R$. For computational efficiency, time-consuming scans in the multi-dimensional control parameter space were performed within the BO basis expansion. The control fields obtained within the BO states serve then as an input for the subsequent analysis within the full numerical solution of the TDSE.
requirement we consider consist of a sequence of ultrashort unipolar electric field “spikes”, satisfying the requirements that superimpose harmonic colours $n\omega$ to the fundamental frequency $\omega$ with appropriate phase $\phi_n$ and amplitude $E_n$. In general, $|E_n| \rightarrow 0$ as $n \rightarrow \infty$. In addition, the envelope function $f(t)$ can be optimized. An example of a HCP used in localization protocols is shown in the right panel.

For discussion and analysis, we extract the following observables: the time-dependent populations $P_i(t) = |\langle \varphi_i|\Psi(t)\rangle|^2$ of states $i$, where the $\varphi_i(x;R)$ are the electronic eigenstates (obtained within the BO approximation), and for analysis of the localization dynamics, the projections onto the coherent superposition states, $P_{r,l}(t) = |\langle \Phi_{r,l}|\Psi(t)\rangle|^2$ with $\Phi_{r,l}(x;R) = \frac{1}{\sqrt{2}}[\varphi_g(x;R) + \varphi_u(x;R)]$, $\Phi_l(x;R) = \frac{1}{\sqrt{2}}[\varphi_g(x;R) - \varphi_u(x;R)]$, where $\varphi_u(x;R)$ is the first excited state with ungerade symmetry. The degree of localization for diatomic molecules is quantified by the (time-dependent) asymmetry coefficient

$$A(t) = \frac{P_l(t) - P_r(t)}{P_l(t) + P_r(t)},$$

assuming values between $-1$ and $+1$, with the sign indicating the direction in which the electron is preferentially localized: localization in the direction of the force of the unipolar peak field of the HCP train (positive fields) yields localization in the left potential well, i.e. $A > 0$. The objective is to maximize $A$ via the application of a genetic algorithm to optimize the control parameters of the pulse train.

### 2.2. Half-cycle pulses

The description of trains of half-cycle pulse for quantum control on the ultrashort timescale has been summarized in our previous paper [17]. Shortly, the trains of half-cycle pulses (HCP) we consider consist of a sequence of ultrashort unipolar electric field “spikes”, satisfying the requirement $\int E(t)dt = 0$. The fields are designed such that they feature a strong peak field in one direction (“kicks”), $E_+(t)$, being accompanied by a low-amplitude long lasting off-set field in opposite direction, $E_-(t)$. Pulse trains down to the attosecond regime can be synthesized by the superposition of harmonic colours [24]

$$E(t) = E_0 f(t) \left( \sum_n E_n \cos(n\omega t + \phi_n) \right),$$

where $f(t)$ is the normalized envelope function, $E_0$ the overall field strength, and $E_n$ the amplitude of the harmonics with phase $\phi_n$. Mixing the fundamental frequency $\omega$ with several higher (even and odd) harmonics and choosing the phases $\phi_n$ properly, a unidirectional HCP train can be formed, Fig. 1. In our simulations, we chose a flat-top envelope function with a smoothed ramp-on and -off. The offset field $E_-(t)$ is given by

$$E_-(t) = -E_0 f(t)/2.$$
3. Numerical results

Using a genetic algorithm, the objective is to find optimally shaped HCP trains which induce the highest possible degree of electron localization in one potential well. Localization is transient for homonuclear molecules (where the two lowest eigenstates are bound), and can be permanent for either non-inversion symmetric heteronuclear or dissociative molecules, where two electronic states are located well below the internuclear barrier such that electronic dynamics can “freeze out” \[17,22\]. We mainly search for pulse trains inducing electron localization in the left potential well, corresponding to the direction of force from the kicks. However, localization in the opposite direction along the direction of the quasi-static DC field is possible as well, as we will demonstrate below. The genetic algorithm optimizes the fundamental frequency $\omega$, the field strength $E_0$, the absolute phase of the generating fundamental pulse $\phi_{\text{abs}}$, and the rise time $\tau$, corresponding to the time needed to reach the maximum value of the flat-top envelope (Fig. 1 (b)). The length of the pulses is kept constant and the width of the kicks was fixed to 0.2 $T$ (or 570 as). The optimization by the genetic algorithm is performed within the BO expansion for computational efficiency, however, all results presented here have been obtained from the fully coupled nuclear-electronic Schrödinger equation (eq. 2) using these optimized pulse trains.

3.1. Diatomic potential

We consider first the case of a homonuclear molecule (inversion-symmetric potential):

$$V(x, R) = \frac{1}{R} - \frac{1}{\sqrt{(x \pm R/2)^2 + \alpha(R)}}.$$  \hspace{1cm} (8)

All electronic eigenstates have inversion symmetry, making (inversion-symmetry breaking) localization possible only in the presence of an HCP. The efficiency in forming a transiently localized wavepacket depends on the energy gap between two nearby eigenstates of opposite inversion symmetry \[22\]. We first concentrate on the diatomic model potential for which the excitation gap to the first excited state is very small (compared to the fundamental frequency of the field) and the equilibrium internuclear distances in those two states is very similar (mass = proton mass). The smoothing function $\alpha(R)$ entering the nuclear-electron potential (eq. 1) is parameterized as follows:

$$\alpha(R) = \begin{cases} 
    a e^{-(R-r_1)^2/a_1^2} & R < R_c \\
    b + \frac{c}{1 + e^{-(R-r_2)^2/a_2^2}} & R \geq R_c 
\end{cases}$$

(9)

with $a = 0.6055$, $r_1 = 5$, $a_1 = 4.24$, $b = 0.6$, $c = 0.825$, $r_2 = 6.75$, $R_c = 5$ and $a_2 = 0.35$, yielding potential curves as depicted in Fig. 2 (b).

The parameters of the optimal pulse train are as follows: field strength $E_0 = 0.024$ a.u., rising time $\tau$ of two optical cycles, wavelength 949 nm, and phase $\phi_{\text{abs}} = 0$ (i.e. one HCP spike is located directly at the position where the ramp-on of the envelope has reached its maximum), see Fig. 3 (a). For the flat-top pulse, the total pulse length is of minor importance. We chose a longer pulse in order to demonstrate that localization can be sustained for several vibrational periods. As we have shown recently \[22\], the electronic density distribution is transiently localized on the left nucleus (in the direction of the “kicks”) during the ramp-on (Fig. 3 (b)). The timing and strength of the first kicks is decisive for the success of the control process. After the end of the pulse train, localization of the charge density is oscillating between the two nuclei with an oscillation period inversely proportional to the energy gap between the electronic ground and excited states. With the excitation of the electronic wavepacket, also a vibrational (nuclear) wavepacket, starting from the ground state, is initiated (modulation with a timescale of 18 fs). Population analysis shows that population of higher lying electronic states, as well as ionisation,
are negligible (< 0.6%). A high degree of localization can be achieved: more than 80 % of the population can be driven into the state \( \Phi_l(x; R) \), corresponding to \( A \approx 0.6 \).

The electron localization is due to the interplay between the kicks and the quasi-dc field: almost adiabatic electronic dynamics driven by the quasi-dc offset field with almost impulsive kicks inducing transitions. The field strength of the HCP train plays a dominant role for this non-perturbative dynamics.

We explore the quantum control landscape by studying the dependence of the localization on the pulse parameters. As to be expected for strong-field-driven molecular dynamics, the field strength plays a crucial and non-trivial role in the efficient control of localization. Fig. 4 (a) displays the time-averaged asymmetry \( \bar{A} \), with

\[
\bar{A} = \langle A(t) \rangle_t = \frac{1}{T} \int_0^T A(t) \, dt, \tag{10}
\]

as a function of the field strength \( E_0 \). As was the case for the asymmetry in \( \text{H}_2^+ \) [17], scanning the field strength \( E_0 \) (keeping the other pulse parameters fixed) changes the value of \( \bar{A} \) dramatically: a field strength of \( E_0 = 0.024 \) a.u. yields the highest value of \( \bar{A} = 0.6 \). Decreasing or increasing the field strength reduces the asymmetry substantially, and may even invert the direction of localization. In contrast, the wavelength has a minor influence on \( \bar{A} \) (panel (b)).

The phase (or the timing of the first kicks) plays a crucial role, see Fig. 4 (c). If we apply the same field as before but change the absolute phase by \( \pi \), i.e. the kicks are shifted in between the ones of the best result, none of the kicks manages to transfer a substantial amount of population selectively. However, Fig. 4 indicates that localization in the direction opposite to the direction of the fields should be possible. We have therefore redefined the objective to find an optimally shaped pulse train which induces the highest possible degree of localization in the potential well opposing the direction of the force of the kicks. The optimal pulse train has the following parameters: field strength \( E_0 = 0.029 \) a.u., rising time \( \tau \) of two optical cycles, wavelength 855 nm, and phase \( \phi_{\text{abs}} = 0.76 \pi \). The dynamics of the system driven by the “anti-optimal” field is shown in Fig. 5. Here, too, the localization is determined with the first two kicks. However, as the field strength \( E_0 \) is higher for this case, the first kick does not invert the field dressed
Figure 4. Dependence of the time-averaged asymmetry $\bar{A}$ (eq. 10) on (a) the field strength $E_0$, (b) the fundamental frequency, and (c) the absolute phase $\phi_{\text{abs}}$.

Figure 5. Early dynamics of the system driven by the two HCP trains: (a) Populations $P_l(t)$, $P_r(t)$ with driving HCP train (b) leading to localization in the direction of the kicks. Panels (c,d) display the corresponding dynamics and field for localization in the opposite direction. The full field, together with the electron density $\rho(x,t) = \int |\Psi(x,R,t)|^2 dR$ is displayed on the right column for the case of localization in the direction opposing the kicks.

population, and the system stays in the lower field dressed state, periodically disturbed by the kicks.

3.2. Localization in a model system with four nuclei
Efficient localization dynamics can be also found for chain-like molecules. For demonstration purposes, we restrict ourselves to a simplified test system with frozen nuclear coordinates, mimicking a four-atomic linear molecule. The one-electron Hamiltonian is given by

$$H = \hat{T}_x - \frac{1}{\sqrt{(x \pm R/2)^2 + \alpha}} - \frac{2}{\sqrt{(x \pm 3R/2)^2 + \alpha}}.$$  \hspace{1cm} (11)

The internuclear distance is fixed to $R = 4$ a.u., and the screening parameter $\alpha$ is set to 1. Figs. 6,7 show two different scenarios where the electron is efficiently localized in the left potential well: in the first case (Fig. 6), the HCP train pushes the electron density which is initially localized in the two outer potential wells from the right well over the internuclear barrier to the left potential well, thereby populating intermediately the third and fourth excited state. After the end of the pulse, the system is in a superposition of the first lowest lying
eigenstates. In the second case (Fig. 7), the HCP train simply ionizes the electron out of the right potential well (thereby creating a superposition between mainly the first two lowest lying electronic states).

**Figure 6.** Left panel: Electronic potential and lowest eigenstates of a model system with four nuclei. Upper right panel: electronic density $\rho(x,t)$, driven by an optimized pulse train in the lower panel. The lower panel also displays the asymmetry $A(t)$. The pulse train leaves the system in a coherent superposition of electronic states.

While this reduced system does not fully describe the charge transfer in chain-like molecules as the vibrational motion is not included, the example suggests that controlled charge migration in larger systems is possible and proceeds under similar conditions as we have analyzed for the diatomic molecules.

**4. Summary and conclusion**

We have presented numerical simulations examining the quantum control of electronic dynamics in small molecules using trains of unidirectional half-cycle pulses (HCPs) on the few femtosecond scale. Such trains consist of narrow unidirectional “peaks” and a weak offset field in the opposite direction. Extending our recent work [17,22], the systems we have analysed here are representing di- and four-atomic molecules.

We explore the quantum control landscape by scanning different pulse parameters describing localization in a diatomic model potential. In the diatomic model system, the almost static offset component of the field shapes field-dressed BO potential curves. Between the kicks, the system adiabatically follows the dressed states, while the HCPs induce almost impulsive couplings between the states. The timing and strength of the first kicks during the ramp-on of the field is decisive for the outcome of the localization dynamics: depending on the pulse parameters, localization in direction of the kicks but also in the direction opposite to the kicks is possible.

Efficient electron localization can be also found in longer, chain-like molecules. In a simple model system representing a four-atomic molecule with frozen nuclei, we were able to demonstrate that these quantum control protocols can be readily extended towards longer chain-like molecules. Interesting applications are e.g. electron localization in molecules, resembling
chains of atoms, where one functional group or atom has an excited dissociative channel. By steering the electron along the chain, one atom or functional group can be detached in a controlled way. In order to examine this class of processes, electron localization / transport along a chain of atoms with bound excited states with coupled nuclear dynamics needs to be considered. Although for the homonuclear diatomic molecules localization exists only in the presence of the field, this is a necessary precursor for the implementation of charge transfer along chain-like molecules. Transient polarization can induce a molecular electronic current from one end of the chain to the other. Furthermore, detachment of selected functional groups via electron localization and bond breaking can be envisioned. Transient electron localization can be probed via the asymmetry in the photoelectron distribution induced by a weak, attosecond XUV pulse [22, 25].

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References
[1] Zewail A H 2000 Angew. Chem., Int. Ed. Engl. 39 2586–2631
[2] Warren W S, Rabitz H and Dahleh M 1993 Science 259 1581–5694
[3] Shapiro M and Brumer P 2003 Principles of Quantum Control of Molecular Processes (New York: Wiley)
[4] Rice S A and Zhao M 2000 Optical Control of Molecular Dynamics (New York: Wiley)
[5] Brixner T, Damrauer N H and Gerber G 2001 Adv. At. Molec. Opt. Phys. 46 1–54
[6] Dantus M and Lozovoy V V 2004 Chem. Rev. 104 1813–1859
[7] Wollenhaupt M, Assion A and Baument T 2004 Femtosecond Laser Pulses: Linear Properties, Manipulation, Generation and Measurement (Heidelberg: Springer)
[8] Krausz F and Ivanov M 2009 Rev. Mod. Phys. 81 163–234
[9] Dudovic N, Smirnova O, Levesque J, Mairesse Y, Ivanov M Y, Villeneuve D M and Corkum P B 2006 Nature Phys. 2 781
[10] Mairesse Y, Dudovic N, Levesque J, Ivanov M Y, Corkum P B and Villeneuve D M 2006 New J. Phys. 10 025015
[11] Sola I J, Mvel E, Elouga L, Constant E, Strelkov V, Poletto L, Villoreisi P, Benedetti E, Caumes J P, Stagira S, Vozzi C, Sansone G and Nisoli M 2006 Nature Phys. 2 319
[12] Kling M F, Siedschlag C, Verhoef A J, Khan J I, Schultze M, Uphues T, Ni Y, Uiberacker M, Drescher M, Krausz F and Vrakking M J J 2006 Science 312 246
[13] Geppert D, von den Hoff P and de Vivie-Riedle R 2008 J. Phys. B: At. Mol. Phys. 41 074006
[14] Tong X and Lin C D 2007 Phys. Rev. Lett. 98 123002
[15] Grae S and Ivanov M Y 2007 Phys. Rev. Lett. 99 163603
[16] Grafe S and Ivanov M Y 2008 J. Mod. Opt. 55 2557
[17] Persson E, Burgdörfer J and Grafe S 2009 New J. Phys. 11 105035
[18] Calvert C R, Bryan W A, Newell W R and Williams I D 2010 Phys. Rep. 491 1
[19] He F, Ruiz C and Becker A 2007 Phys. Rev. Lett. 99 083002
[20] He F, Ruiz C and Becker A 2008 J. Phys. B: At. Mol. Phys. 41 081003
[21] Grafe S and Engel V 2006 Chem. Phys. 329 118–125
[22] Persson E, Pichler M, Wachtler G, Hirsch T, Jakubetz W, Burgdörfer J and Grafe S 2011 Phys. Rev. A 84 043421
[23] Feit M D, Fleck J A and Steiger A 1982 J. Comput. Phys. 47 412–433
[24] Persson E, Schiessl K, Scrinzi A and Burgdörfer J 2004 Phys. Rev. A 74 013818
[25] Grae S, Engel V and Ivanov M Y 2008 Phys. Rev. Lett. 101 103001