



Local control approach to ultrafast electron transfer



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ABSTRACT

We study ultrafast electron transfer between separated nuclei using local control theory. By imposing electron ionization and electron transport through the continuum, different local control formulations are used to increase the yield of retrapping the electron at the desired nuclei. The control mechanism is based on impulsive de-excitation. Both symmetric and asymmetric nuclear arrangements are analyzed, as well as the role of the nuclear motion.

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1. Introduction

In recent years, advances in laser technology enabled the production of sub-femtosecond (*i.e.* attosecond) pulses, with frequencies in the UV regime, paving the way to the development of a new scientific domain, called Attosecond Physics [1,2]. These pulses are so short that ionization or Auger processes can be in principle resolved in real time; alternatively, their bandwidths are large enough that several electronic states can be coherently excited at the same time. Currently, attophysics techniques are mainly used as a spectroscopic tool, to unravel ultrafast molecular (or condensed phase) processes, by means of *e.g.* pump–probe techniques.

One can observe several analogies with the field of Femtochemistry [3], where the pump–probe scheme was successfully used to resolve the nuclear dynamics. After monitoring the motion of nuclei, a natural step forward was to attempt to control the nuclear dynamics [4], which was proposed both in the time and energy (frequency) domain. In the first case, the control can be seen as the search for an external, often phase-modulated field, $\mathcal{E}(t)$, such that a transition from the initial state $|\psi_i\rangle$ to a predefined target state $|\psi_f\rangle$ at a time t_f is induced and typically maximized. The target state can imply the preparation of a new chemical species, for instance, through the fragmentation of a particular bond.

In achieving this goal, one may distinguish two different strategies, optimal control theory [5] (OCT) and local control theory [6] (LCT). In OCT, the control fields are constructed employing information on the entire dynamics from time t_i to time t_f , whereas in LCT, the field is determined instantaneously, taking the system's

response into account. Different local control schemes have found many applications in molecular physics [7–23].

The main purpose of this work is to apply local control techniques to attosecond processes, involving the motion of electrons. The control of the electron processes is a challenge due to the velocity at which the electron moves and disperses, particularly when the electron ionizes. However, attosecond pulses can be seen as the ideal tools, acting very locally in time and offering wide bandwidth to span both continuum and bound states. Presently, the experimental techniques that allow to modulate attosecond pulses are not yet developed. However, the theoretical anticipation is timely, as it helps determining the physical resources that might be necessary in order to exert this control.

Within this scientific context, our goal is to control the electron transfer between two separated protons, mainly aided by local control methods. This elementary process can constitute an important step toward the control of many chemical reactions involving charge rearrangement. In this work the electron transfer is not mediated by nuclear motion. Hence, it relies on fast processes through the ionization continuum. The essential step involves the photoassociation of the electron colliding with the target proton. In some respects, this work complements studies of photoassociation between neutral atoms in slow collision [24,25].

One ultimate motivation is to determine the laser resources necessary to enhance the yield of reversible quantum transitions between bound states and ionized states, which is an essential ingredient in attophysics [1,2]. Our work should be regarded as a tentative step towards that goal as we use simplified models where the electron is treated in a single dimension.

The paper is organized as follows. In Section 2 we introduce the model Hamiltonian and describe the numerical methods applied to interpret the control mechanisms. In Section 3 we investigate under which conditions one can maximize electron transfer

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between two protons largely separated within the framework of local control theory. We consider impulsive ultrafast processes that occur in few femtoseconds. We also analyze the effect of the nuclear dynamics onto the yields. Finally, Section 4 is the conclusions.

2. Numerical methods

We need to use a consistent model for treating both continuum and bound electronic states in a system with a single electron and two nuclei. As a first approximation, we use a 1-D Hamiltonian, where the electron is constrained to move in the molecular axis z driven by a linearly polarized external field, $\mathcal{E}(t)$. Neglecting small mass polarization terms, the Hamiltonian in the length gauge is (atomic units are used throughout unless otherwise stated)

$$H = -\frac{1}{2} \frac{d^2}{dz^2} + V(z, R) + z\mathcal{E}(t) \quad (1)$$

For this reduced dimensional study the internuclear distance R is fixed and the electron-nuclei potential is modeled by a soft-core Coulomb potential [26]

$$V(z, R) = -\frac{Q_1}{\sqrt{(z+aR)^2 + \varepsilon_1^2}} - \frac{Q_2}{\sqrt{(z-bR)^2 + \varepsilon_2^2}} + \frac{Q_1 Q_2}{R} \quad (2)$$

where Q_i are the nuclear charges ($Q_{He} = 2$ and $Q_H = 1$ a.u.), a and b account for the relative distances of the nuclei with respect to the center of mass, and ε_i are smoothing parameters. In the case of H_2^+ , $a = b = 1/2$ whereas for e.g. HeH^{2+} , $a = m_p/(m_p + m_x) = 0.2012$ and $b = m_x/(m_p + m_x) = 1 - a = 0.7988$ [27]. The smoothing parameters were chosen as $\varepsilon_1 = \varepsilon_2 = 1$ for H_2^+ and $\varepsilon_1(He) = 0.705$, $\varepsilon_2(H) = 1.414$ for HeH^{2+} .

This model has been extensively applied as a first qualitative step to analyze ionization processes in H_2^+ and high-harmonic spectra [28,29], as well as electron-nuclear dynamics [30–33]. One can easily extend the calculation to include the nuclear motion by removing the constraint in R and by adding the internuclear kinetic energy, as explained later. For the laser-controlled dynamics shown in this work, the 2-D calculations give quantitatively the same results as the 1-D model. Initially, we assume a fixed nuclei approximation, where an hydrogen atom and a proton, or the He and H nuclei, are largely separated. Two different ways to achieve electron transfer applying LCT are considered. In the first one, the objective is mathematically expressed as the population in a target state $|\psi_f\rangle$, constructed as a wave function localized at the nuclei where we want the electron to be recaptured.

Defining the projector $P_T = |\psi_f\rangle\langle\psi_f|$, the rate of population transfer into the target state is

$$\begin{aligned} \frac{d}{dt} \langle P_T \rangle &= i \langle [H(t), P_T] \rangle = i \mathcal{E}(t) \langle [-\mu, P_T] \rangle \\ &= \mathcal{E}(t) 2\Im \{ \langle \Psi(t) | \mu | \psi_f \rangle \langle \psi_f | \Psi(t) \rangle \} \end{aligned} \quad (3)$$

Hence, a control field of the form

$$\mathcal{E}(t) = \lambda \Im [\langle \Psi(t) | \mu | \psi_f \rangle \langle \psi_f | \Psi(t) \rangle] \quad (4)$$

where \Im stands for the imaginary part and $\Psi(t)$ is the wave function of the system, guarantees monotonic increase in time of population in the target state [34,35].

In the second LC protocol, we minimize the energy of the electron once it moves out in the ionization continuum, such that the electron can be stopped and retrapped in the further nuclei. A sufficient condition to reduce the energy of the system upon the interaction with an external field is that the expectation value of H_0 (the Hamiltonian in the absence of the external field) decreases as a

function of time or, equivalently, that its time derivative (the energy rate) is lower than zero. Using the time dependent Schrödinger equation (TDSE) the rate is evaluated as

$$\begin{aligned} \frac{d}{dt} \langle H_0 \rangle &= i \langle [H(t), H_0] \rangle = i \mathcal{E}(t) \langle [-\mu, T] \rangle \\ &= \mathcal{E}(t) \frac{1}{i2m} \left\langle \left(\frac{d^2 \mu}{dz^2} + 2 \frac{d\mu}{dz} \frac{d}{dz} \right) \right\rangle \end{aligned} \quad (5)$$

In the special case of a linear dipole moment, i.e., $\mu = qz$ (with q being a constant), Eq. (5) takes the simple form

$$\frac{d}{dt} \langle H_0 \rangle = \mathcal{E}(t) \frac{q}{m} \langle p \rangle \quad (6)$$

Hence, one can reduce the energy of the system choosing a field proportional to the expectation value of the momentum [36–38],

$$\mathcal{E}(t) = \lambda f(t) \langle \Psi(t) | p | \Psi(t) \rangle \quad (7)$$

with $\lambda < 0$.

In both cases λ enters as a free parameter that measures the strength of the laser interaction. λ is found numerically by trial and error. In Eq. (7) we include a positive sine square envelope function $f(t)$ that forces a time-delay in the action of the control field, to avoid minimizing the energy before the electron has time to fly over the outer nuclei.

In the homonuclear (symmetrical) system, one has to take superpositions of the ground and the first excited electronic states of the Hamiltonian in order to construct the initial and target localized states,

$$\psi_{L_1/R_1} = (\psi_1 \pm \psi_2) \quad (8)$$

where ψ_{L_1} is the lowest energy wave function localized at the left proton (left potential well) of Eq. (2) and ψ_{R_1} is the target wave function localized at the right potential well.

In general, in our simulations we assume that the initial state is already excited, that is, ψ_L is multiplied by an exponential factor that gives an initial momentum in the positive direction

$$\Psi(z, 0) = \psi_{L_1}(z) e^{ik_0 z} \quad (9)$$

In addition, to initiate the LCT approach one needs a small “seed” of population in the right potential well (the target state), which we fix as $\approx 0.3\%$. Once the local control field is found, this “seeded” population is no longer needed, and the simulations shown in the results imply 100% population in the ground (localized) state at initial time.

The numerical results are obtained by solving the TDSE with the Split-Operator method [39–41] with time steps of $\Delta t = 0.01$ a.u. A grid of 256 points spanning from $z = -80$ to $z = 80$ a.u. is used for the electronic coordinate. Imaginary (“optical”) potentials [42,43] absorb the outgoing wave functions avoiding reflection on the grid boundaries and allowing to measure the ionization probability. The eigenstates $\psi_{1,2}$ from Eq. (8) are computed using the Fourier Grid Hamiltonian method [44]. The dynamical mechanism of the transfer is studied by analyzing the approximate phase-space representation of the wave functions at different times, using the Husimi transformation [45].

Finally, to study the role of the nuclear motion in the control of the electron transfer, 1 + 1D calculations were performed using the full Hamiltonian of Eq. (1) including the nuclear kinetic term. The initial wave packet is then the product of the electronic wave function times a nuclear Gaussian wave packet $\psi_{nuc}(R)$, centered at the left nuclei.

In this case, we use a grid of 1024 points ranging from $R = 0.1$ to $R = 150$ a.u. for the nuclear coordinate and 256 points from $z = -80$ to $z = 80$ for the electronic coordinate.

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