Chemical Physics Letters 698 (2018) 152–156

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper

Tunneling induced electron transfer between separated protons

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ARTICLE INFO

Article history:
Received 20 November 2017
In final form 11 March 2018
Available online 13 March 2018

Keywords:
Femtosecond pulses
Quantum control
Electron transfer
Tunneling
Local control theory

ABSTRACT

We study electron transfer between two separated protons using local control theory. In this symmetric system one can favour a slow transfer by biasing the algorithm, achieving high efficiencies for fixed nuclei. The solution can be parametrized using a sequence of a pump followed by a dump pulse that lead to tunneling-induced electron transfer. Finally, we study the effect of the nuclear kinetic energy on the efficiency. Even in the absence of relative motion between the protons, the spreading of the nuclear wave function is enough to reduce the yield of electronic transfer to less than one half.

1. Introduction

Quantum control can be described as a dynamic process that prepares coherent superpositions of Hamiltonian eigenstates manipulating the amplitudes and relative phases [1–3]. When this wave function involves several electronic states, the phases typically oscillate in the sub-femtosecond (hence attosecond) time scale. However, this is not always the case, as energy differences between Rydberg states vary on the order of $\sim 1/n$ Hartrees, which can be relatively small for large n. Hence the period of motion associated to these phase oscillations can be of the order of femtoseconds or larger [4,5].

In molecules, other scenarios of electronic changes associated to the femtosecond scale exists whenever the electronic states become quasi-degenerate. This is the case in the proximity of conical intersections [6–8], and it is also the case in the dissociation limit, where many molecular electronic states correlate with the same atomic (or fragment) electronic states. The latter situation is particularly interesting in symmetric arrangements. Then the initial and target wave function may only differ by the phase of the initial superposition, which identifies different isomers that can be converted via tunneling [9,10]. However, the similar time scales of vibrational and electronic motion can make the control of the electronic processes particularly sensitive to the nuclear displacements or even require fully correlated electron-nuclear motion [11,12]. Electronic processes in the attosecond regime may be more protected against vibrational motion, particularly if the process occurs a single time [13]. However, the effect of vibrational decoherence must still be carefully studied [14,15].

In this work we investigate electronic transfer between two separated protons, where the electron is initially in a single proton, breaking the symmetry of the system. We have recently shown that a local control (LC) approach [16–18] can be used to find ultrashort pulses that induce electron transfer in very few femtoseconds, yielding pulses characterized by a prominent (very intense) spike that maximizes the probability of retrapping the electron at the desired proton, after moving and spreading in the ionizing continuum [13]. In principle there are infinite solutions of the control problem, and the LC method is flexible enough to find different types of solutions. In this work we show that for particular choices of observables, varying the initial conditions can lead to optical control of electron transfer that explore a different control mechanism, characterized by slow electron transfer via tunneling.

The paper is organized as follows. In Section 2 we introduce the model Hamiltonian and describe the numerical methods. In Section 3.1 we show the results of local control for fixed nuclei and describe the control mechanism. In Section 3.2 we study the effect of the nuclear motion on the transfer efficiency. 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 protons. As a first approximation, we use a $(1+1)$D Hamiltonian, including the internuclear distance R and the electron

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https://doi.org/10.1016/j.cplett.2018.03.016
0009-2614/

separation to the center of mass z, where the electron is constrained to move in the molecular axis. For this reduced dimensional study the inter-particle interaction is modeled by a soft-core Coulomb potential [19]. In the presence of a linearly polarized external field, $\mathcal{E}(t)$, and neglecting small mass polarization terms, the Hamiltonian in the length gauge is (atomic units are used throughout unless otherwise stated)

$$H = -\frac{1}{2}\frac{\partial^2}{\partial z^2} - \frac{1}{M}\frac{\partial^2}{\partial R^2} + V(z,R) + z\mathcal{E}(t) \tag{1}$$

where M is the mass of the proton, with the soft-core Coulomb potential

$$V(z,R) = -\frac{1}{\sqrt{1+(z-R/2)^2}} - \frac{1}{\sqrt{1+(z+R/2)^2}} + \frac{1}{R} \tag{2}$$

This model has been extensively applied as a first qualitative step to analyze ionization processes in H_2^+ and high-harmonic spectra [20,21], as well as electron-nuclear dynamics [11,12,22,23].

Initially, we assume a fixed nuclei approximation, where an hydrogen atom and a proton are largely separated. In Section 3 we show electron transfer applying LCT. The objective is mathematically expressed as the population in a target state $|\psi_f\rangle$, constructed as a wave function localized at the proton where we want the electron to be recaptured [24,25]. Therefore, the control field depends on the projection on a target state

$$\mathcal{E}(t) = \lambda\Im\left[\langle\Psi(t)|\mu|\psi_f\rangle\langle\psi_f\Psi(t)\right] \tag{3}$$

where $\Im$ stands for the imaginary part and $\Psi(t)$ is the wave function of the system. Here λ enters as a free parameter to be found numerically, that characterizes the strength of the laser interaction.

In finding the local control field with Eq. (3), the projection operator $P_t = |\psi_f\rangle\langle\psi_f|$ must commute with the Hamiltonian of the system [17]. Therefore, the target wave function must be an eigenfunction of the Hamiltonian. However, if the separation of the protons is not large enough, the localized wave functions are not true eigenstates, as the tunneling time cannot be neglected. One way of solving this problem is to add a very small static field component, $\mathcal{E}_{DC}$, that breaks the symmetry of the Hamiltonian, such that the effective potential is tilted, $V_{\text{tilted}}(z) = V(z) + z\mathcal{E}_{DC}$. Then the target state and the initial state are the ground and first excited electronic wave functions of the Hamiltonian with the DC component localized at the desired proton. The initial state, ψ_{L_1}, is localized at the left potential well while the target state, ψ_{R_1}, is localized at the right potential well. By making $\mathcal{E}_{DC}$ small enough, the tilted potential has no significant impact on the search of the local control field for large internuclear distances ($R \geqslant 20$ a.u.). However, the DC component is an essential ingredient in the control of electron localization at smaller proton separations.

In addition, to obtain better results from LCT, we add a small excitation to the initial electronic wave function in the form of a small net momentum in the positive direction, $\Psi(z,0) = \psi_{L_1}(z)\exp(ik_e z)$. The numerical procedure to integrate the TDSE and apply LCT is described in detail in [13].

3. Slow electron transfer

3.1. The tunneling mechanism

We first study electron transfer using LCT using the projection (Eq. (3)), when the electron starts with a small positive average momentum of $k_e = 0.001$ a.u. The results of a typical LCT calculation are shown in Fig. 1(a) and (b) for fixed nuclei separated $R = 10$ and $R = 20$ a.u. In the latter case, a free electron (without any acting force) would take roughly $t = R/k_e = 2\cdot 10^4$ a.u. ≈ 500 fs to cross the distance, but the initial kinetic energy is not enough to overcome the Coulomb potential of the atom, so that the LC pulse must first excite the electron and then retrap it at the right-side proton. As explained in Section 2, the calculations must be performed adding a static field. We show the optimal fields and overall populations in the left and right domains (the basins of the left and right protons),

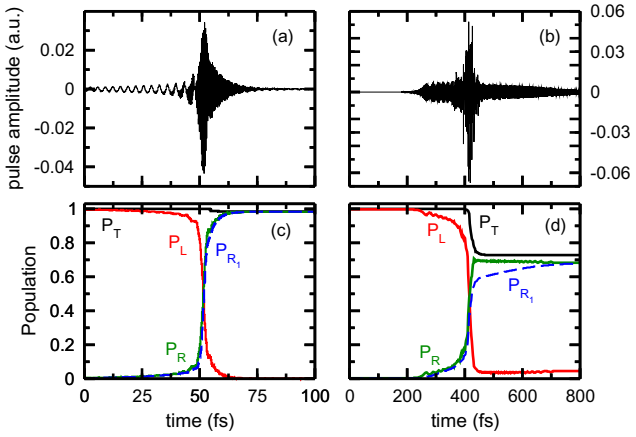

Fig. 1. Laser control fields and population dynamics for an internuclear distance of 10 a.u. [(a) and (c)] and 20 a.u. [(b) and (d)], when tunneling is the main mechanism responsible for electron transfer.

$$P_D(t) = |\langle\Psi(z,t)|\Psi(z,t)\rangle_{z\in D}|^2 \tag{4}$$

where D is $(-L/2, 0)$ for the left domain and $(0, L/2)$ for the right one, with L the grid size. We also show the yield of the control, measured as the overlap of the wave function with the target state, $P_{R_1}(t) = |\langle\psi_{R_1}|\Psi(z,t)\rangle|^2$.

For $R = 10$ a.u., full electron transfer is achieved with $\sim 0.08\%$ population remaining in the left potential well. All the population in the right proton at final time is localized in the target state, so $P_{R_1}/P_R = 1$, an there is no population loss due to ionization. For $R = 20$ a.u., again the electron transfer is almost perfect, with $\sim 6\%$ population in the left hydrogen and $P_{R_1}/P_R = 0.99$, while the remaining population (less than 30%) is lost as ionization.

To interpret the mechanism for the electron transfer, it is important to notice that the average energy of the electron never exceeds the energy of the Coulomb barrier between the two protons. In addition, at these internuclear distances, the tunneling times between localized states are within the time-scale of the dynamics. A rough calculation for $R = 20$ a.u. gives $t_1 \approx 3$ ps for population inversion between the ground localized states, ψ_{L_1} and ψ_{R_1}, and $t_2 \approx 250$ fs for population inversion between the first excited localized states in each well, ψ_{L_2} and ψ_{R_2}. With $R = 10$ a.u., the population inversion between ψ_{L_1} and ψ_{R_1} is $t_1 \approx 100$ fs.

Roughly, we propose the following mechanism as the key process governing the electron transfer controlled by the LC pulse: first, as a net positive momentum is given to the electron initially, the electron finds itself distributed between the excited states of the left hydrogen with energies below the continuum. The electron is then transferred to the right proton by tunneling. Finally, the pulse takes energy away from the electron sitting in the right proton, effectively stopping the back-tunneling process to the left proton. This mechanism is consistent with the fact that in the momentum representation, the electron distribution remains practically centered around $p = 0$ at all times.

Since tunneling is the main mechanism behind the control process, in the following we impose such mechanism by choosing sine squared ($\sin^2(\pi(t-t_0)/\tau)$) shaped pulses that lead the different