Quantum Dynamics

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Periodic Electron Circulation Induced by Circularly Polarized Laser Pulses: Quantum Model Simulations for Mg Porphyrin**

*Ingo Barth and Jörn Manz**

Dedicated to our wives Tanja and Etsuko

During the last two decades, femtosecond laser pulses in the time domain from about five to several hundred fs (1 fs = 10^{-15} s) have been used for analysis and control of molecular reaction dynamics, supplemented by quantum simulations and predictions of the laser-driven nuclear wavepacket dynamics.[1–5] The recent advent of even shorter laser pulses from about one hundred attoseconds (1 as = 10^{-18} s) to a few fs has opened an analogous field of research, namely, the analysis and control of electron dynamics in the time domain in which the nuclei are essentially frozen.[6] The first purpose of the work described here was to design corresponding circularly polarized laser pulses to induce periodic unidirectional circulation of electronic wavepackets in ring-shaped molecules such as Mg porphyrin (see Figure 1).

Our work has been motivated by stimulating experimental and theoretical work in this field, including observations of ultrafast motions of electrons in atoms,[6] and quantum simulations of the measurement of periodic intramolecular electron transfer (PIET),[7] by means of high harmonic generation (HHG),[7–9] analogous to the tomographic imaging of molecular orbitals.[10] PIET may be expressed in terms of a coherent electronic wavepacket representing a "hybrid" superposition $(0,e)$ of the electronic ground (0) and excited (e) states, with energies E_0 and E_e, equal populations $P_j = |C_j|^2 = 0.5$ $(j = 0,e)$ and period $\tau_{e,0} = h/(E_e - E_0)$ [Eq. (1)].

$$|\Psi_{0,e}(t)\rangle = C_0|\Psi_0\rangle e^{-iE_0t/\hbar} + C_e|\Psi_e\rangle e^{-iE_et/\hbar} \quad (1)$$

Note that the preparation of periodic electron dynamics, for example, PIET, by means of few cycle laser pulses, has not been described in Ref. [7] or elsewhere.[30] The second purpose of our research was, therefore, to design laser pulses for the preparation of "hybrid"-type electronic states, analogous to Equation (1).

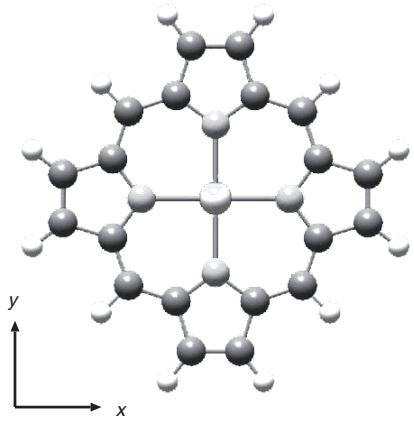

Figure 1. View of Mg porphyrin in the x/y plane. The laser pulse propagates out along the z axis.

Control of electronic motions by means of few cycle laser pulses has also been predicted[11,12] and demonstrated,[13] in particular for electronic population transfer from an initial electronic wave function to a final one by means of so-called "π pulses". The population dynamics for electronic wavepackets driven by π pulses is equivalent to that for nuclear ones (compare Refs. [12] and [14]). This analogy provides another motivation for our work. In Ref. [15] (compare with Ref. [16]) we designed circularly polarized π and π/2 pulses for specific complete or half population transfers, respectively, in oriented racemates such that ultimately the chirality of the laser pulse is transferred into that of nuclear wavepacket dynamics that yields pure enantiomers. In this paper, we shall show that the chirality of circularly polarized laser pulses can be transferred to unidirectional electron circulation, using analogous π/2 pulses as a reference.

As an example, we consider the Mg-porphyrin molecule oriented in the x/y plane (e.g. as achieved by means of laser pulses[7,10,17]), see Figure 1. The x and y components of the electric fields of four representative right circularly polarized laser pulses propagating along the z axis [Eqs. (2) and (3)]

$$\mathscr{E}_x(t) = \mathscr{E}_0 s(t)\cos(\omega t) \quad (2)$$

$$\mathscr{E}_y(t) = \mathscr{E}_0 s(t)\sin(\omega t) \quad (3)$$

with shape function [Eq. (4)] and intensities $I(t) = \varepsilon_0 c \mathscr{E}_0^2 s(t)^2$

$$s(t) = \sin^2\left(\frac{\pi t}{t_p}\right), \quad 0 \le t \le t_p \quad (4)$$

are plotted in Figure 2. The parameters are listed in the caption of Figure 2. The short pulse durations (full width at half maximum of the intensity) $\tau = 0.364\,t_p$ correspond to broad spectral widths $\Gamma = 3.295\,\hbar/\tau$. The resulting coherent

[*] I. Barth, Prof. Dr. J. Manz
Institut für Chemie und Biochemie
Freie Universität Berlin
Takustrasse 3, 14195 Berlin (Germany)
Fax: (+49) 30-838-54792
E-mail: jmanz@chemie.fu-berlin.de

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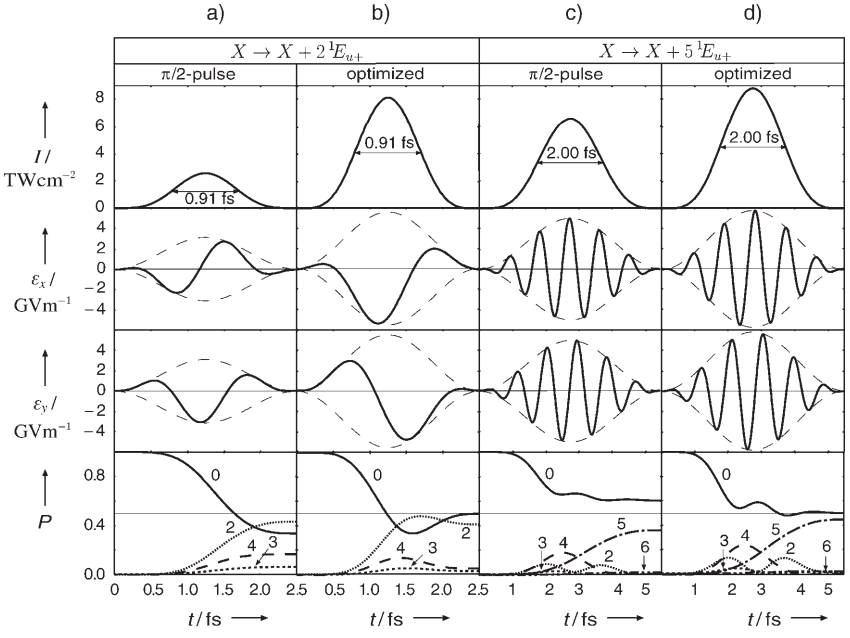

Figure 2. Circularly polarized π/2 and reoptimized π/2 laser pulses for half population transfer from the electronic ground state $X = 1\,^1A_{1g}$ to excited target states $2\,^1E_{u+}$ and $5\,^1E_{u+}$. The four rows show the time evolutions of the intensities, the *x* and *y* components of the electric fields, and the resulting populations of the ground (0) and excited states $j\,^1E_{u+}$ ($j = 2,\ldots,6$), respectively. The parameters of the laser pulses shown in columns (a), (b), (c), (d) are $\mathscr{E}_0 = 3.11$, 5.54, 4.98, and 5.77 GV m^{-1}, and $\hbar\omega = 2.66$, 1.94, 4.56, and 4.40 eV, respectively.

electronic wavepackets are calculated as solutions [Eq. (5)] of

$$|\Psi(t)\rangle = \sum_j C_j(t)|\Psi_j\rangle e^{-iE_jt/\hbar} \tag{5}$$

the time-dependent Schrödinger equation [Eq. (6)] starting

$$i\hbar|\dot{\Psi}(t)\rangle = (\mathscr{H}_{el} - \underline{\mathscr{E}}(t)\underline{M})|\Psi(t)\rangle \tag{6}$$

from the initial ($t = 0$) electronic ground state, $|\Psi_0\rangle = |\Psi_X\rangle$, $X = 1\,^1A_{1g}$, and using the semiclassical electronic dipole approximation. In Equations (5) and (6), $|\Psi_j\rangle$ denote the electronic eigenfunctions of the time-independent Schrödinger equation [Eq. (7)] with electronic Hamiltonian operator $\mathscr{H}_{el}$ (assuming fixed nuclei as shown in Figure 1) and with electronic eigenenergies E_j. Equivalently, we propagate Equation (8) for the time-dependent coefficients $C_j(t)$ and

$$i\hbar\dot{C}(t) = H(t)C(t) \tag{8}$$

corresponding populations $P_j(t) = |C_j(t)|^2$ of electronic states j, with matrix elements $H_{ij}(t) = -\underline{\mathscr{E}}(t)\langle\Psi_i|\underline{M}|\Psi_j\rangle e^{-i(E_j-E_i)t/\hbar}$, starting from $C_j(t{=}0) = \delta_{j0}$. For reasons of molecular symmetry, the right circularly polarized laser pulses with maximum intensities below 10^{13} W cm^{-2} yield exclusive population transfer from the electronic ground state $|\Psi_0\rangle$ to excited states $|\Psi_j\rangle = |\Psi_{j^1E_{u+}}\rangle = (|\Psi_{j^1E_{u,x}}\rangle + i|\Psi_{j^1E_{u,y}}\rangle)/\sqrt{2}$. The corresponding electronic energies E_j and matrix elements $\langle\Psi_0|\underline{M}|\Psi_j\rangle$ of the six j^1E_u states are adapted from quantum chemistry CASPT2 and TD-DFT results of Rubio et al. ($j = 1,\ldots,4$)[18] and Sundholm ($j = 5,6$),[19] respectively.

Our previous experience[15] suggests π/2 pulses for half population transfer from the initial ground state $|\Psi_0\rangle$ to a specific target state $|\Psi_j\rangle = |\Psi_{j^1E_{u+}}\rangle$. By analogy, the laser parameters should satisfy Equation (9), where $M = \max|\langle\Psi_0|\underline{M}|\Psi_{j^1E_{u+}}\rangle\mathscr{E}(t)|/\mathscr{E}_0$. Figure 2a,c

$$\frac{M\mathscr{E}_0 t_p}{\hbar} = \frac{\pi}{2} \tag{9}$$

show the π/2 pulses, designed exemplarily for selective half population transfers from $|\Psi_X\rangle$ to $|\Psi_{2^1E_{u+}}\rangle$ or $|\Psi_{5^1E_{u+}}\rangle$, within one or two cycles during $\tau = 0.91$ fs and 2.00 fs and with corresponding spectral widths $\Gamma = 2.38$ eV and 1.08 eV, respectively, together with the resulting population dynamics. As anticipated, the final populations of the initial and target states are indeed close to each other, but with significant deviations from the goal [$= 0.5$, see Eq. (1)], due to the rather broad spectral widths which cover several neighboring levels with the same symmetry, j^1E_{u+}, allowing their temporary populations. Fortunately, this deficiency may be compensated by reoptimizing the laser parameters ω and $\mathscr{E}_0$, starting from the π/2 pulses as a refererence. The "reoptimized π/2 pulses" and population dynamics are shown in Figure 2b,d, demonstrating preparations of almost perfect periodic "hybrid" electronic states [see Eq. (1)], $|\Psi_{X,2^1E_{u+}}\rangle$ and $|\Psi_{X,5^1E_{u+}}\rangle$, with corresponding periods $\tau_{2^1E_{u+},X} = 1.55$ fs and $\tau_{5^1E_{u+},X} = 0.91$ fs, respectively.

Thus, we have achieved the second goal of this paper. At the same time, we also reach the first one, that is, preparation of periodic unidirectional electron circulation. This is demonstrated by snapshots of the dynamics of the electronic wave packet after the laser pulse. Figure 3 shows the corresponding difference $\Delta\rho(t) = \rho(t) - \rho(0)$ of the resulting single electron density at time t after the laser pulse, minus the initial density, exemplarily for half population transfer from $|\Psi_X\rangle$ to $|\Psi_{5^1E_{u+}}\rangle$. Apparently, the optimized right circularly polarized π/2 pulse with period $2\pi/\omega = 0.94$ fs yields net right, periodic circulation of the shifted electron density $\Delta\rho(t)$, with a nearly identical period $\tau_{5^1E_{u+},X} = 0.91$ fs.

In conclusion, the present quantum simulations show that the chirality of the reoptimized π/2 right circularly polarized laser pulses may be transferred to state-selective right unidirectional net electron circulation. The unidirectionality is a consequence of selective preparation of hybrid states $|\Psi_{X,j^1E_{u+}}\rangle$ in the preoriented molecule. Likewise, the corresponding left circularly polarized laser pulses induce analo-

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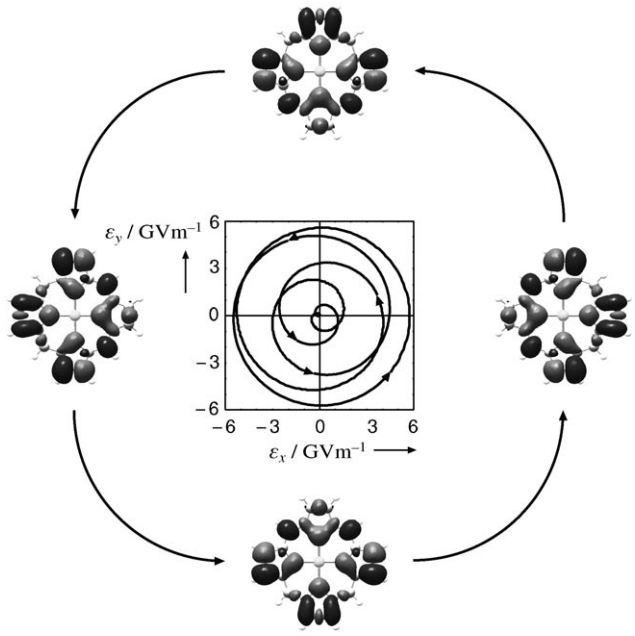

Figure 3. Reoptimized right circularly polarized $\pi/2$ laser pulse designed for half population transfer from the electronic ground state $X=1\,^1A_{1g}$ to the target state $5\,^1E_{u+}$, and the resulting periodic right electron circulation. The x and y components of the electric fields are shown as a polar plot (cf. Figure 2d). The electron circulation is illustrated by snapshots of the difference $\Delta\rho(t)$ of the single electron density $\rho(t)$ minus the initial density $\rho(0)$, at time $t=5.67$ fs and $t+k\tau_{5^1E_{u+},X}/4$, $(k=1,2,3,...)$ with $\tau_{5^1E_{u+},X}=0.91$ fs. The target state $|\Psi_{5^1E_{u+}}\rangle$ corresponds to the $3e_{g+}$ to $2b_{1u}$ orbital transition (weight = 94%).[19] As a consequence, $\Delta\rho(t)$ may be approximated in terms of the (partial) transition of a single active electron, essentially from $3e_{g+}$ to $2b_{1u}$.

gous left unidirectional net electron circulation, represented by $|\Psi_{X,j^1E_{u-}}\rangle$. Similar ignitions of electron circulation are favored by molecular symmetries with degenerate representations of molecular states, for example, other ring-shaped molecules, or linear molecules which should support ignition of toroidal-type electron circulations, on a molecular scale, that is, much more compact and faster than circulation of Rydberg electrons along Kepler orbits around atoms.[20,21] The effect may be observed for example, by means of high harmonic generation, cf. Refs. [8,10,22,23], depending on special selection rules due to the symmetry of the molecule,[24] or by time-dependent asymmetric photoelectron spectra as suggested in Refs. [25,26].

Conservation of angular momentum implies that unidirectional electron circulations may be coupled to vibrational pseudorotations (Jahn–Teller effect, see also Ref. [27]) and to rotations of the molecular frame in the time domains beyond 100 fs and even picoseconds, respectively.[28] This is in accord with the present assumption of frozen nuclei in the sub-5 fs time domain. In contrast, extensions of the present scenario to longer pulse durations could call for simulations of nonfrozen nuclei, for example, they might move away from the Franck–Condon domain towards domains with different transition frequencies. This may be compensated by adequate chirping of the laser pulses.[11,29] In any case, it is advantageous to employ laser pulses with durations close to one or very few electronic cycles (e.g. $\tau \leq 2$ fs in the present case) because they support many electronic cycles before decay, for example, by coupled nuclear motions.

Moreover, by analogy with the results of Ref. [15], one may also design reoptimized π pulses for complete population transfer from the ground to excited electronic states $|\Psi_{j^1E_{u+}}\rangle$. These target states present stationary electronic ring currents instead of the present periodic electron circulation. Combinations of sequential reoptimized $\pi/2$ and π pulses could prepare excited hybrid states, for example, $|\Psi_{4^1E_{u+},5^1E_{u+}}\rangle$, with different periods, for example, $\tau_{4^1E_{u+},5^1E_{u+}}$.

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