

Controlling excitonic wavepacket motion in the PS1 core-antenna system

B. Brüggemann*, V. May

Institut für Physik, Humboldt-Universität zu Berlin, Newtonstr. 15, 12489 Berlin, Germany

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Abstract

Sub-picosecond laser pulse driven localization of electronic excitation energy is suggested for a biological chromophore complex. Based on an exciton model of the photosynthetic core antenna PS1 of *Synechococcus elongatus* the shape of the respective laser pulse is calculated using optimal control theory combined with a density matrix theory accounting for energy relaxation and dephasing caused by the protein environment. As a target observable we choose the population oscillation after photo-excitation between the two Chlorophylls forming the special pair. The temperature dependence of the related control yield is studied as well as its dependence on the pulses duration.

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1. Introduction

The combination of a liquid-crystal or opto-acoustic femtosecond laser pulse shaper with a feedback from the outcome detection has been demonstrated to be a powerful tool for addressing various control tasks (cf. for example [1–3]). Although originally concentrated on small molecules in gas-phase, meanwhile examples for the pulse control of the dynamics of polyatomic systems as well as of condensed phase systems [4,5], and even biological systems [6] have also been reported.

A standard scheme of laser pulse control is the attempt to form a certain vibrational wavepacket which guides the whole molecule into the required target state. Recently we presented computational studies on the laser pulse control of an electronic wavepacket formed by Frenkel excitons [7]. This has been done for a small and structurally well-defined biological chromophore sys-

tem, the monomeric FMO-complex of the photosynthetic antenna system of green bacteria (cf. e.g. [8]). To achieve excitation energy concentration into one of the seven Bacteriochlorophyll molecules of this complex one has to prepare a coherent superposition $\sum_{\alpha} A(\alpha)|\alpha\rangle$ of the different delocalized exciton states $|\alpha\rangle$. This superposition should correspond (in the ideal case) to the excited state $|m\rangle$ of the complex, where only the m th molecule has been excited. Of course, this simply represents the inversion $|m\rangle = \sum_{\alpha} C_{\alpha}^{*}(m)|\alpha\rangle$ of the definition of exciton states (the $C_{\alpha}(m)$ denote the expansion coefficients of the exciton states in the site basis). It has been discussed in [7] how to construct from this picture the shaped laser pulse which drives the system into the particular target state $|m\rangle$ and how to improve this simple and direct attempt by optimal control theory (OCT). As a precondition of laser pulse control of exciton dynamics we discussed in [7] the need of a chromophore complex with a well balanced distribution of excitonic oscillator strengths. With other words, it is necessary to have a system where all transition dipole matrix elements \mathbf{d}_{α} of the different exciton states are of a comparable magnitude. Systems with high spatial symmetry do not fulfill this requirement and, hence, are less suited

* Corresponding author. Present address: Chemical Physics, Chemical Centrum, Lund University, P.O. Box 124, 22100 Lund, Sweden. Fax: +46462224119.

E-mail addresses: ben.bruggemann@chemphys.lu.se (B. Brüggemann), may@physik.hu-berlin.de (V. May).

for such studies. Additionally, we demonstrated in [7] that even upon inclusion of two-exciton states, energy dissipation, dephasing, spatial averaging, and energetic disorder the controllability of the excitation dynamics is not completely lost. Studying the dependence of excitation energy localization on these additional disturbances it turned out to be essential to vary the overall laser pulse intensity and the pulse duration for the best result.

It is the aim of the present Letter to show that laser pulse control of excitation energy dynamics is possible even in much larger systems. One possible candidate for such studies would be the Photosystem 1 (PS1) of *Synechococcus elongatus* containing 96 Chlorophyll molecules (Chl). The PS1 structure resolution has been recently improved [9] leading to a sufficient detailed knowledge of the spatial position as well as the mutual orientation of all pigments. As in our former studies we will concentrate on the so-called Q_y -excitations of the Chls, known to form delocalized exciton states which may be excited by photons in the optical range. Several approaches exist to formulate an exciton model of these transitions in PS1 [10–13]. We will use the results of our own studies (see [13]). All 96 Chl site energies have been defined by simultaneously using low temperature absorption, linear dichroism and circular dichroism spectra as inputs to an evolutionary algorithm. An independent calculation of time-dependent fluorescence spectra allowed to adopt the coupling of the exciton states to vibrational degrees of freedom (mainly of the dissipative protein environment). The related exciton relaxation takes place on a time-scale extending from a few 100 fs up to about 20 ps [14–17]. Although this limits the time window for the control task, control of the dynamics should be possible for selected target states. As our studies on the FMO complex in [7] showed, at weak and intermediate excitation intensities two-exciton states only have a minor influence on the control yield. The possible neglect of the two-exciton manifold is essential for the PS1 since it covers 4560 levels at best. Furthermore spectral inhomogeneities are relatively weak and of less importance, and, finally, the oscillator strength for the absorption in the Q_y -region is distributed across all exciton levels.

For such a large system as the PS1 there are many ways to define target states. Their significance, of course depends on the possibility to detect the matching of the target by the driven excited state in an experiment (cf. the discussion in [18]). Up to now, there have been a few experiments demonstrating coherent excitonic features in the time domain for different pigment protein complexes, among them B820 [19], and FMO [20]. Considering, e.g., the purified bacterial reaction center of *Rhodobacter sphaeroides* at room temperature, oscillatory behavior in the time dependent anisotropy could be measured after a 80 fs excitation pulse (see [21]). By

applying the theoretical framework of [22], this oscillation has been assigned to the formation of a coherent superposition of excitonic states at the special pair (two coupled Bacteriochlorophylls acting as the primary electron donor in the charge transfer chain). Following this experiment we will demonstrate that using an appropriately shaped pulse a population of only one Chl of the special pair at target time is possible. At later times this will lead to a damped oscillation of the population between the two Chls, and will show up in the anisotropy caused by the different orientations of their dipole moments.

The Letter is organized as follows. In the following section we give a short overview on the theoretical description. This is followed by the study of different control tasks. The results are discussed in the last section.

2. Optimal control theory of exciton dynamics

In order to describe the Q_y -excitations of the 96 Chls found in the PS1 of *S. elongatus* we apply our recently developed exciton model [13], as it has been described in the introduction.

As already underlined and discussed in more detail in [7] the inverted definition of exciton states $|\alpha\rangle$, i.e., $|m\rangle = \sum_x C_x^*(m)|\alpha\rangle$ may be used as a first guideline in searching for a laser pulse which moves an excitonic wavepacket into a specific local excitation $|m\rangle$. But it needs some time to prepare such a state during which dephasing may act. Therefore, a more involved description is needed which is given by OCT for open quantum systems as described in [23,24] (see also references therein).

OCT translates the search for the laser pulse, which drives the considered system to a particular state (the target state $|\phi_{\text{tar}}\rangle$) at a particular time t_f , into an extremum search for a special functional (see, e.g. [1]). Once this has been put into the correct theoretical frame it results a nonlinear functional equation for the radiation field (its electric field component $\mathbf{E}(t)$). The solution gives the *optimal* pulse, i.e., the pulse which solves the control task. This equation reads

$$\mathbf{E}(t) = \frac{i}{\hbar\lambda(t)} \text{tr}_x \{ \hat{\sigma}(t; \mathbf{E}) [\hat{\mu}, \hat{\rho}(t; \mathbf{E})]_- \}. \quad (1)$$

The trace expression on the right-hand side has to be taken with respect to the states of interest, here the PS1 electronic ground-state $|0\rangle$ and all 96 (single) exciton states. Besides the dipole operator $\hat{\mu}$ referring to the Q_y -excitations of all Chls of the PS1 the trace includes the (reduced) density operators $\hat{\sigma}(t)$ and $\hat{\rho}(t)$. The latter describes laser driven dynamics of the PS1 Frenkel-excitations (including energy relaxation and dephasing) and is governed by the following equation of motion (quantum master equation, see e.g. [25]):

$$\frac{\partial}{\partial t} \hat{\rho}(t) = (-i\mathcal{L}_0 - \mathcal{D} - i\mathcal{L}_{\text{field}}(t))\hat{\rho}(t). \quad (2)$$

The Liouville superoperators \mathcal{L}_0 , \mathcal{D} and $\mathcal{L}_{\text{field}}(t)$ are responsible for the free exciton motion, dissipation, and the coupling to the laser pulse, respectively. As an initial state for the density operator one takes $\hat{\rho}(t_0) = |0\rangle\langle 0|$, i.e., before the action of the laser pulse the system is in its electronic ground-state.

In contrast to the standard propagation of $\hat{\rho}$ starting at t_0 and ending at t_f the density operator $\hat{\sigma}(t)$ is propagated backwards in time starting at t_f with the ‘initial’ condition $\hat{\sigma}(t_f) = |\phi_{\text{tar}}\rangle\langle\phi_{\text{tar}}|$. The equation of motion is similar to that for $\hat{\rho}$ but with $-\mathcal{D}$ replaced by a quantity which has to be separately adopted to the backward propagation (for more details see [23,24]). However, different choices of the dissipative part lead to similar results during our numerical simulation, among them $+\mathcal{D}$, $+\mathcal{D}^\dagger$, and the neglect of dissipation. The propagation of the two density operators is coupled via the electric field. If it is replaced by the expression on the right-hand side of Eq. (1) we have two coupled nonlinear equations which can be solved iteratively. To carry out the iteration we start with a Gaussian shaped field at a certain guessed wavelength for the first backward propagation. Then, one can iterate the set of equations back and forth for a fixed number of times, or until a certain convergence criterion has been fulfilled. The overall time dependence of the field amplitude is determined by the Lagrangian parameter $\lambda(t)$, chosen in a way that it is centered at $(t_f - t_0)/2$ and that it nearly vanishes for $t = t_0$ and $t = t_f$.

3. Results and discussion

Using the iterative scheme mentioned in the preceding section the optimal pulse is calculated which drives the system from the electronic ground state (present at $t = t_0$) into the target state at $t = t_f$. However, we cannot expect a complete solution of the control task. The presence of dissipation avoids that $\hat{\rho}$ matches the pure state density operator $|\phi_{\text{tar}}\rangle\langle\phi_{\text{tar}}|$, i.e., the control yield $\langle\phi_{\text{tar}}|\hat{\rho}(t_f)|\phi_{\text{tar}}\rangle$ remains smaller than 1 in any case. To reach the maximum yield, on the one hand it is advisable to decrease the temperature to reduce the effect of dissipation. On the other hand, it is also reasonable to change t_f , and in this manner to adapt the possible pulse duration to the internal dynamics of the PS1.

As the first step we will discuss which chromophores are suitable as target sites. On the one hand, the successful application of the OCT for the Chls forming the main absorption band is obstructed by fast relaxation and dephasing processes combined with the small energetic splittings of the relevant exciton levels. On the other hand, the lower exciton levels are subject to slower

dissipation processes. Furthermore they are spectrally well separated, what makes the Chls forming these states ideal candidates for the control scheme. In our model of the PS1 [13] the lowest exciton states are formed by the trimers and dimers B31–B32–B33 (lowest energy), A31–A32–B7, A38–A39 and S1–S2 (special pair). It turned out, that due to its linear chain symmetry the trimer B31–B32–B33 could only be excited collectively (not its Chls independently). As this can be easily achieved by an Gaussian pulse matching the energy of the lowest exciton-state, we did not investigate this trimer any further. Depending on the polarization of the exciting laser pulse, better results could be achieved for the excitation of single chromophores of the trimer A31–A32–B7. However it turned out that the Chls of the dimers A38–A39 and S1–S2 were the most suitable targets for the Optimal Control approach giving both reasonable absolute populations of the chromophores as well as a good ratios of the population of the optimized to the other chromophore in the dimer.

In the following, we will concentrate on the dimer S1–S2, the special pair, since the results can be compared with the coherent excitation of the special pair of the bacterial reaction center of [21]. Fig. 1 presents an example for the optimal pulse as well as the population dynamics at 77 K and an optimization time of $t_f - t_0 = 200$ fs. Since the Chls of the special pair are strongly coupled the population oscillates between both. But when t_f is reached a maximal population of the target Chl is achieved (solid line). Additionally, the increasing population of the lowest contributing exciton level is shown. It is the state, where both Chls are equally populated. A damping of the oscillations results from a vanishing of the coherences between this eigenstate and the other eigenstates related to the special pair.

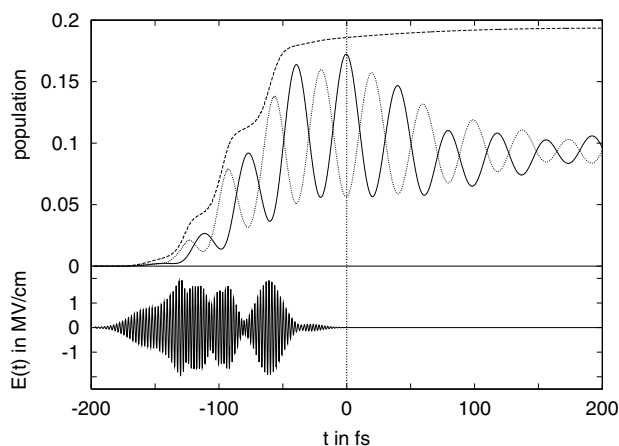


Fig. 1. Time evolution of the populations for the optimal field at 77 K, optimization time is 200 fs, and target time is 0 fs. Population of the two single Chls in the P700 (solid and dotted), and population of one low-lying excitonic eigenstate (dashed) which is mostly localized on the P700. In the lower panel the electric field is given.

Although it is not possible here to achieve a stable population of the chosen target state the obtained oscillations between two Chls offer a way to detect the result of the laser pulse control as they can be measured using the transient anisotropy. To maximize these oscillations we define the population difference of the two localized states at each Chl of the special pair as the efficiency of our control attempt. Fig. 2 displays this efficiency for different duration $t_f - t_0$ of the control pulse and for temperatures from 4 K up to room temperature. In this figure, the two competing factors which limit the control yield can be studied. To spectrally select the relevant exciton states relatively long pulses are needed ($\gg 1$ ps). However due to the strong dissipation all coherences are lost after a relatively short time ($\ll 1$ ps). A reasonable compromise has to be found for each temperature, the result is given by the maxima of the control yield in Fig. 2. Decreasing the temperature leads to a remarkable increase of the maximal control efficiency (it can be fitted by an exponential law with temperature constant of 113 K). The best suited duration $t_f - t_0$ of the control pulse increases also drastically with decreasing temperature (it can be fitted by an exponential law with temperature constant of 620 K). According to these dependencies, the position of the maximum follows a power law (dotted line in Fig. 2). At higher temperatures shorter pulses are necessary to reach the decreased maximal efficiency. For comparison, also Gaussian pulses of different frequencies and durations have been used, giving the maximal efficiency of 0.02 at 4 K. This is also the efficiency in the limit of very short pulses in Fig. 2, since then all structures of the pulses have vanished.

The optimal pulses for different temperatures are shown in Fig. 3. The time resolved spectrum of the pulse for 77 K is given as a contour plot in Fig. 4. All pulses have in common a spectral shift from 700 to 625 nm at early times. This leads to coherences between the eigen-

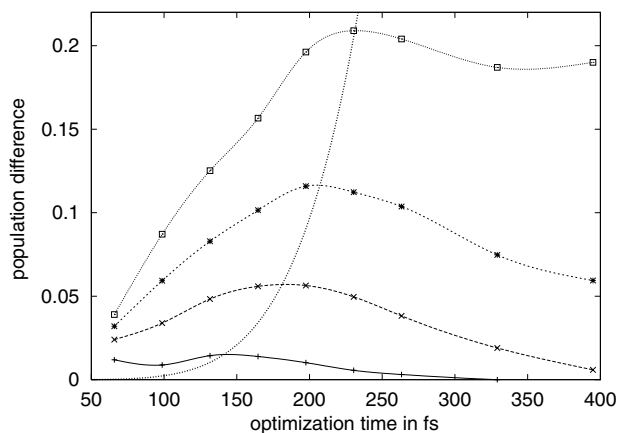


Fig. 2. Difference of the populations of the two P700 Chl for the optimal pulse at the target time. The X-axis gives the used optimization time. The temperatures are 4 K (dotted), 77 K (dashed), 150 K (long-dashed), and 295 K (solid). A dotted line connects the position of the maxima.

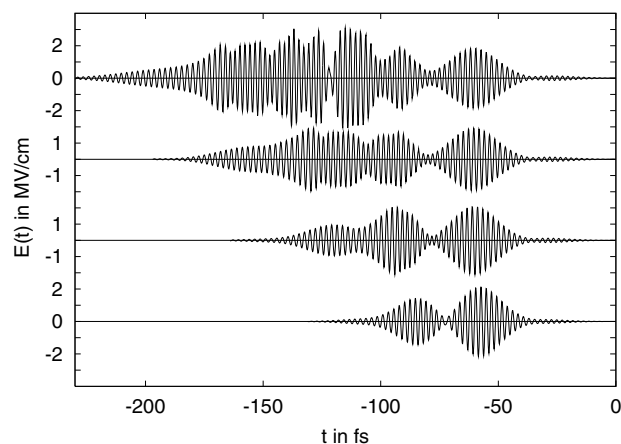


Fig. 3. The optimal field for different temperatures, from top to bottom: 4, 77, 150 and 295 K. The target time is set to zero, and the optimization time is given by Fig. 2.

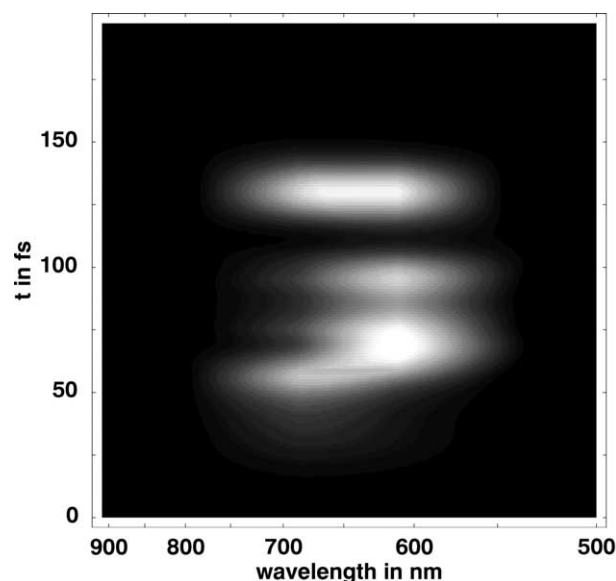


Fig. 4. Contour plot of the time resolved spectrum of the optimal pulse for $T = 77$ K.

states used to build up the target state. Additionally, a broad range of other eigenstates is populated. The following pulses de-excite these unwanted states and shift the excitation to the target state. This is achieved by up to two pulses at 625 nm, and a broad pulse at the end of the optimal pulse, which appears for all studied temperatures (note that in our PS1 model the lowest wavelength is 650 nm, therefore the pulses at 625 nm in Fig. 4 correspond to two phase shifted pulses with higher wavelengths).

4. Conclusions

It has been shown in this Letter, that the suggestion of spatial excitation energy localization in chromophore

complexes of [7] can be extended to larger systems like the PS1, although a proper selection of the target state is necessary. As observable we choose the oscillations of the transient anisotropy caused by the coherent oscillation of the population between the two Chls of the special pair. In comparison with the experimental results [21] for the special pair of the bacterial Reaction Center, where after a Gaussian excitation oscillations in the transient anisotropy could be measured even at room temperature, it is predicted that these oscillations can be increased dramatically using lower temperature as well as shaped laser pulses. This represents a new way investigate the time dependence of coherences in dissipative systems.

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