§6. Design of Optimal Microwave Pulses to Enhance Molecular Orientation: Development of Optimal Control Simulation Algorithms

Ohtsuki, Y.
(Dept. Chem., Grad. School Sci., Tohoku Univ.)

Quantum optimal control theory (OCT) provide a general and flexible tool for designing a control to best manipulate a dynamical system [1]. The control design equations are derived by maximizing or minimizing a cost functional that measures control achievement. As the control design equations are nonlinear coupled equations, the development of efficient solution algorithms is essential to perform OCT-based simulations. For this purpose, monotonically convergent algorithms have been developed, in which a dynamical system is assumed to linearly interact with a control [2]. There exist dynamical systems in which nonlinear interactions with respect to a control play a crucial role. Examples include the control of molecular orientation/alignment by using strong electric fields such as laser pulses and microwave pulses.

In order to apply OCT-based simulations to the molecular orientation/alignment control, we develop a new family of monotonically convergent algorithms [3]. For the sake of providing concrete descriptions, we consider a 3D quantum rigid rotor model that interacts with a microwave pulse, $E(t)$, with a linear polarization. The molecular system is initially in the ground electronic and vibrational state. We assume that the frequencies of a microwave are low enough to solely induce rotational transitions. Taking into account the lowest order induced dipole interaction, effective Hamiltonian is expressed as

$$H^{t} = BJ^2 - \mu E(t) - [(\alpha_{\parallel} - \alpha_{\perp})\cos^2\theta + \alpha_{\perp}]\frac{[E(t)]^2}{2} \qquad (1)$$

Here B is the rotational constant, J is the angular momentum operator, and θ is the polar angle between the polarization vector of $E(t)$ and the molecular axis. The polarizability component parallel (perpendicular) to the molecular axis is denoted by $\alpha_{\parallel}$ ($\alpha_{\perp}$). The time evolution of the system is described by a density operator, $\rho(t)$. In the double-space representation, the quantum Liouville equation is written as

$$i\hbar\frac{\partial}{\partial t}|\rho(t)>=\{L - ME(t) - A[E(t)]^2\}|\rho(t)> \qquad (2)$$

where $M \leftrightarrow [\mu,\cdots]$ $A \leftrightarrow \frac{1}{2}[(\alpha_{\parallel} - \alpha_{\perp})\cos^2\theta + \alpha_{\perp}]$, etc.

An optimal pulse is defined by the pulse that maximizes or minimizes a cost functional that quantitatively expresses a control objective. If two Hermitian operators, X and $Y(t)$, are introduced to specify a target state at a specified final time, t_f, and an intermediate target over the control period, the cost functional is typically expressed as

$$J =< X|\rho(t_f)> + \int_0^{t_f} dt < Y(t)|\rho(t_f)> - \int_0^{t_f} dt \frac{[E(t)]^2}{\hbar\lambda(t)} \qquad (3)$$

where a positive function, $\lambda(t)$, weighs the physical significance of the penalty [1].

We have developed a family of monotonically convergent algorithms to iteratively solve the optimal control problems given by Eq. (3) under the constraint of Eq. (2) [3]. The key idea is to divide the control into two identical components and to introduce auxiliary steps to up date each component at every iteration step. Then, all the expressions associated with control in the control design equations are represented by the symmetrical sum of products of the identical components. It guarantees that the two control components approach the same control when the iteration converges.

We apply the newly developed simulation to the orientation control of HCN, whose rotational period is 14ps [3]. In the following numerical results, time is measured in units of the rotational period, where by the electric field is expressed as a dimensionless form, $\mu E(t)/B$. Our aim here is to achieve the orientation control at a specified final time 15 with the target operators, $X = \cos\theta$ and $Y(t) = 0$. To assure smooth rise and decay of a microwave pulse, we set $\lambda(t) = \lambda_0 \sin(\pi t/2\Delta)$ for $0 < t < \Delta$, $\lambda(t) = \lambda_0$ for $\Delta < t < t_f - \Delta$ and $\lambda(t) = \lambda_0 \sin(\pi(t_f - t)/2\Delta)$ for $t_f - \Delta < t < t_f$ with $\lambda_0 = 10$ and $\Delta = 2$. To clearly see the effects of the polarizability on the orientation control, we assume a fictitious model molecule that has 10000 (Fig. 1) and 100000 (Fig. 2) times larger values for the polarizability components. In the former case (Fig.1), the results are virtually the same as those obtained using the original values. On the other hand, the optimal pulse in Fig. 2 is characterized by a highly asymmetric structure. The asymmetric interaction induced by an such an asymmetry leads to efficient orientation control. In Fig. 2(b), the degree of orientation has a value of 94.2% at the final time when it is assessed by using $X = \cos\theta$.

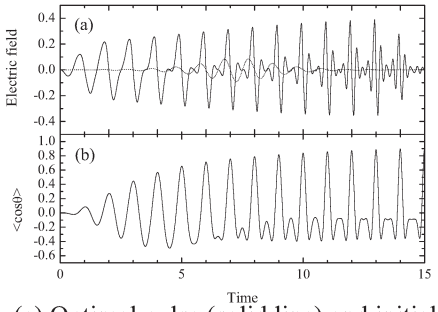

Fig. 1. (a) Optimal pulse (solid line) and initial trial (dotted line) and (b) target expectation value as a function of time [3].

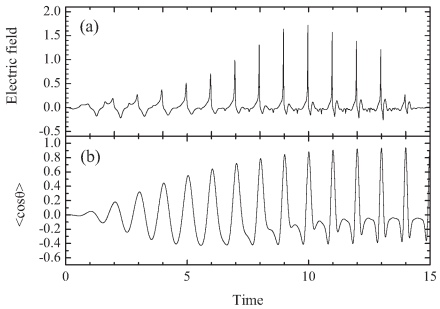

Fig. 2. (a) Optimal pulse and (b) target expectation value [3].

1) Y. Ohtsuki et al., J. Chem. Phys. **120**, 5509 (2004) and references therein.
2) Y. Ohtsuki et al., Phys. Rev. A **75**, 033407 (2007).
3) Y. Ohtsuki and K. Nakagami, Phys. Rev. A **77**, 033414 (2008).