Nonadiabatic Transitions and Laser Control of Molecular Processes

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Abstract. Nonadiabatic transitions play crucial roles in various dynamic processes in physics, chemistry, and biology. This is true also for laser control of molecular dynamics. In this lecture, I will first explain the importance of nonadiabatic transitions together with the basic theories and then demonstrate how various molecular processes can be controlled by manipulating lasers. Actually, by controlling nonadiabatic transitions among dressed states, we can control various molecular processes.

WHAT IS NONADIABATIC TRANSITION?

Nonadiabatic transition is a transition between adiabatic states caused by a variation of the adiabatic parameter. This is a highly multi-disciplinary concept, being an origin of the mutability of this world [1]. Potential energy surface crossing is the most typical example, governing various dynamic processes, and is described by the time-independent theory of nonadiabatic transition. On the other hand, transitions induced by external time-dependent fields are treated by the time-dependent theory of nonadiabatic transition.

The most basic model was first discussed by Landau, Zener, and Stueckelberg independently in 1932. The Landau-Zener formula or the Landau-Zener-Stueckelberg theory is well known. This theory has, unfortunately, many defects and cannot work well in the physically and chemically important regions. After 60 years, we have successfully obtained a complete set of solutions which can be directly applied to practical problems (see the references in [1]). This is called Zhu-Nakamura theory.

FLOQUET STATE REPRESENTATION AND NONADIABATIC DYNAMICS

Molecular processes in a time-dependent laser field can be described by the following Schrödinger equation:

\[ i \frac{d \Psi}{dt} = H \Psi = [H_0 + \mu \epsilon(t) \cos(\omega(t)t + \phi(t))] \Psi, \]  

(1)
where $\mu$, $\epsilon(t)$, $\omega(t)$, and $\phi(t)$ are the dipole operator, laser intensity, laser frequency, and phase, respectively. Here we use the adiabatic approximation, assuming that the time dependence of laser parameters $X = \{\epsilon(t), \omega(t), \phi(t)\}$ is weaker than the time-dependence of laser itself, and divide the time derivative as

$$\frac{d}{dt} = (\frac{\partial}{\partial t})^X + \dot{X} \frac{\partial}{\partial X}. \tag{2}$$

First, we solve the eigenvalue problem at fixed $X$,

$$i(\frac{\partial}{\partial t})_X \Phi_\alpha = H_\Phi \Phi_\alpha. \tag{3}$$

After taking a time average over the laser period $T$, we have

$$\det[H_\Phi - \lambda I] = 0, \tag{4}$$

where $\lambda_\alpha$ is called quasi-energy, and the Floquet Hamiltonian matrix is given by

$$H_{\alpha,\beta}^F = (E_\alpha - \mu \hbar \omega) \delta_{m,n} \delta_{\alpha,\beta} - (\delta_{m,n+1} + \delta_{m,n-1}) \mu_{\alpha,\beta}/2, \tag{5}$$

where $\alpha$ and $\beta$ designate the molecular state and $\mu_{\alpha,\beta}$ represents the transition dipole moment. The eigenstates obtained from the above equation are called dressed states. They are shifted up or down from the original molecular states by the photon energy, $\hbar \omega$, and deformed by the laser-molecule dipole coupling. This is called dressed-state- or Floquet-state-representation (see for instance, [2]). The nonadiabatic transitions among the dressed states are induced by the time-variations of the laser parameters $X$, and are described by

$$\Psi = \sum_\alpha a_\alpha(X) \Phi_\alpha(t : X) \quad \text{with} \quad \dot{a}_\alpha(X) = -i \sum_\beta a_\alpha(X) \langle \Phi_\alpha | \dot{X} \frac{\partial}{\partial X} | \Phi_\beta \rangle, \tag{6}$$

where

$$\langle \langle \cdots \rangle \rangle = \frac{1}{T} \int_0^T dt < \cdots >. \tag{7}$$

If the laser is not very strong and do not induce violent multi-photon processes, we can use the two-state picture described by the following Hamiltonian:

$$H = \left( \begin{array}{cc} E_1 + \hbar \omega, & -\mu \epsilon(t)/2 \\ -\mu \epsilon(t)/2, & E_2 \end{array} \right). \tag{8}$$

Various theories of time-dependent nonadiabatic transition can be applied in the dressed state representation in order to control molecular processes [1].
FIGURE 1. Complete excitation from $|1\rangle$ to $|3\rangle$ by one and half period of frequency chirping in the four-level model. Time variations of the population (upper part), laser frequency (middle part), and laser envelope (bottom part) are shown. Reprinted in part with permission from [4]. Copyright(2002) American Chemical Society.

VARIOUS IDEAS OF LASER CONTROL OF MOLECULAR PROCESSES

Various ideas of laser control have been proposed so far such as coherent control, adiabatic rapid passage, chirped pulse, pump-dump, pulse-shape driven, STIRAP, and $\pi-$pulse method. Nice summaries can be found in the references [3, 4]. Because of the shortage of space, further description is not provided here. The reader should refer to these books.
OUR NEW IDEAS

We have been proposing two different methods, usage of the complete reflection phenomenon and control by periodic sweeping of laser parameters [1, 5, 6, 7, 8]. The complete reflection phenomenon is a peculiar phenomenon in the case of time-independent nonadiabatic tunneling (NT) type of transition, in which the two diabatic potential curves as a function of spatial coordinate cross with opposite signs of slopes and create a potential barrier in the lower adiabatic potential. By shifting up an attractive ground potential surface by cw laser and creating NT type crossings with a repulsive excited potential, we can control molecular dissociation by properly adjusting the laser frequency and creating the complete reflection condition where we want to stop the dissociation. This idea was demonstrated to work well in the case of one- and two-dimensional models [5]. The second idea is to control the nonadiabatic transition at curve crossing between dressed states by sweeping the laser parameter, for instance the frequency, and realizing the constructive interference for the desirable process [6, 7, 8]. The control conditions can be formulated by using the theory of time-dependent nonadiabatic transition. This scheme has been extended so that the periodic sweeping of laser parameters can be replaced by a sequence of linearly chirped pulses [9]. This is expected to be realized relatively easily, since linear chirping can now be rather commonly used in experiments. This second idea is a generalization of chirping, π—pulse, and adiabatic rapid passage, and can be applied not only with laser but also with any other time-dependent external field.

NUMERICAL EXAMPLES

Various numerical demonstrations based on our ideas have been published in the references cited above. Among them, the selective excitation among closely lying multi-levels by using the periodical sweeping of laser frequency is shown here [8]. The level 1 is the ground level and the other three, 2-4, are the excited states. The level spacings and transition dipole moments are assumed to be \( \omega_{12} = 500 \text{cm}^{-1} \), \( \omega_{23} = \omega_{34} = 10 \text{cm}^{-1} \), and \( \mu_{12} = \mu_{13} = \mu_{14} = 1.0 \text{au} \). Figures 1 demonstrate the complete excitation to the level \( |3> \) with use of one and half period of sweeping. The transition time is about 3ps, which is close to the limit determined by the uncertainty principle. The peak intensity of the laser pulse is 0.5917GW/cm\(^2\). The laser frequency is chirped linearly as follows:

\[
\omega(t) = \begin{cases} 
\omega_{14} + c(t-t_0) & (t \leq t_1), \\
\omega_{14} - c(t-t_2) & (t_1 < t < t_3), \\
\omega_{14} + c(t-t_4) & (t > t_3),
\end{cases}
\]

where \( t_1 = t_0 + \Delta t_1, t_2 = t_0 + 2\Delta t_1, t_3 = t_2 + \omega_{24}/c + \Delta t_2, t_4 = 2t_3 - t_2, c = 346.6 \text{cm}^{-1}/\text{ps}, \Delta t_1 = 726.3\text{fs}, \) and \( \Delta t_2 = 90.08\text{fs}. \) The pulse shape is a combination of hyperbolic tangent functions.

Figures 2 depict the similar results by π—pulse with a similar short pulse duration as that in Figure 1. The pulse shape is a hyperbolic-secant function. The peak intensity is 0.05GW/cm\(^2\). Since the pulse duration is short and thus the band-width is broad, the
transitions to $|2\rangle$ and $|4\rangle$ cannot be avoided and the complete excitation to $|3\rangle$ cannot be attained as in Fig. 1. In order to achieve the complete transfer, one order of magnitude longer time is required, as shown in Fig. 3. The peak intensity in this case is $0.005\text{GW/cm}^2$. The adiabatic rapid passage (ARP) certainly requires further longer time, since two ARP processes, $|1\rangle \rightarrow |2\rangle$ and $|2\rangle \rightarrow |3\rangle$, are required to make the selective excitation from $|1\rangle \rightarrow |3\rangle$. Thus, the present scheme would be quite useful and effective for the systems with fast relaxation.

**FUTURE PERSPECTIVES**

For the experimental realization of our idea of periodic sweeping, it would probably be better to use a sequence of linearly chirped pulses in stead of the quadratic chirping. This
is actually possible as discussed in Ref.[9]. Another problem we have to overcome is the feasibility of applications to multi-dimensional systems. This is true for both complete reflection and periodic sweeping. As for the periodic sweeping, a formulation based on the semiclassical propagation and the semiclassical theory of nonadiabatic transition would be useful.

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