Dynamics of photoexcited states in weakly coupled cells with two-level systems

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Abstract. We calculated the dynamics of photoinduced domain growth in two-dimensional models. When a single molecular cell is excited by a photon, vibronic interaction induces energy transfer to the vibration mode in the cell and subsequently the inter-cell interaction helps energy distribution to the adjacent cells. Since nonadiabtic transition between ground and the excited electronic states within a cell is important to consider the dynamics, we fully quantized the vibrational degree of freedom to solve the time-dependent Schrödinger equation numerically. We show that both the interaction between the relevant vibration modes and the electronic states of different cells is necessary to the domain growth in higher dimensional systems.

1. Introduction

Since photoinduced phase transition in organic charge transfer complex[1] and polymer chains[2] was experimentally observed, lots of experimental and theoretical studies have been performed so as to understand the mechanism of the phenomena as well as to search for the possibility of various types of photoinduced phenomena[3].

Theoretically, it has been considered that the initial processes of these phenomena include a nucleation process in terms of the theory of phase transitions. Hence, the dynamics of the photoexcited state involving various types of interaction should be theoretically clarified to understand the mechanism of the photoinduced phase transitions. The dynamics of photoexcited states in those systems is, however, not easy to calculate, since large number of the degree of freedom should be taken into account. In particular, nonadiabatic transitions are considered to play an important role in the dynamics, and hence quantization of vibrational degree of freedom is required to understand the dynamical aspect of the phenomena.

In the present paper, we calculate the dynamics of domain growth in weakly coupled molecular cells on a uniform lattice. The itinerancy of the electrons is not taken into account, which is appropriate approximation in the case of spin-crossover complex[4], for instance. When an excited state is injected into the system, vibronic interaction induces the energy transfer from electronic degrees of freedom to other ones, and then the excitation energy is distributed to the adjacent cells. Our aim is to study the role of the interactions between vibration modes and/or the electronic states by numerical calculations.
2. Models and Methods

We study the systems composed of weakly coupled molecular cells each of which has two electronic levels coupled with a single vibrational degree of freedom. In the present model, flipping of the electronic states between the ground state and the excited state is regarded as a microscopic nature of the photoinduced domain growth. We also assume that the vibronic coupling helps the ground electronic state in a single cell convert to the excited electronic state in the same cell, and that the diabatic potential energy surfaces for the electronic states cross with each other. Hence, in other words, the present study is concerned with the photoinduced phenomena with structural change. Then, by introducing the nonadiabatic coupling between the diabatic potential energy surfaces, we obtain the adiabatic potential energy surfaces for each molecular cell.

In the present model the nonadiabatic transition between the electronic states plays an important role in the dynamics of photoexcited states of the system, which means that classical treatment of the vibrational mode is not appropriate[5] Thus, we fully quantize the vibration degree of freedom within harmonic approximation.

We also assume that the electrons are localized to each cell, which is an appropriate assumption in the case of spin-crossover complex[4]. In this way we obtain the Hamiltonian employed in the present paper which is described by

\[ \mathcal{H} = \sum_{\vec{r}} \left[ \frac{p_{\vec{r}}^2}{2} + \frac{\omega^2 u_{\vec{r}}^2}{2} + \left\{ \sqrt{2\hbar \omega} s u_{\vec{r}} + \hbar \omega (\varepsilon + s^2) \right\} \left( \sigma_{\vec{r}}^z + \frac{1}{2} \right) + \lambda \sigma_{\vec{r}}^x \right] \]

+ \sum_{\langle \vec{r}, \vec{r}' \rangle} \left\{ \alpha \omega^2 u_{\vec{r}} u_{\vec{r}'} - V \left( \sigma_{\vec{r}}^z + \frac{1}{2} \right) \left( \sigma_{\vec{r}'}^z + \frac{1}{2} \right) \right\}, \quad (1)

where \( p_{\vec{r}} \) and \( u_{\vec{r}} \) are the momentum and the coordinate operators of the vibration degree of freedom at site \( \vec{r} \), respectively. The second sum is taken over the pairs of nearest neighbor cells. In the Fock representation, the eigenstates of the vibration mode at site \( \vec{r} \) is expressed as \( |n\rangle_{\vec{r}} \) with conventional definitions of the creation/annihilation operators. The electronic states are described as \(| \downarrow \rangle_{\vec{r}}\) (ground state) and \(| \uparrow \rangle_{\vec{r}}\) (excited state), and \( \sigma_{\vec{r}}^z \) denotes the Pauli matrices which act on the electronic states at site \( \vec{r} \).

Comparing with previous studies on the spin crossover phenomena[6, 7] and photoinduced phase transitions[8, 9] which considered a similar Ising-like models, we stress that it is important to introduce various types of intersite interaction, e.g., \( \alpha \) and \( V \), in order to induce the conversion of the electronic states of unexcited cells, particularly in higher dimensional systems.

Before showing the calculated results, We discuss the values of the parameters. Although the nonadiabatic coupling between the electronic states results in the mixing of \(| \uparrow \rangle \) and \(| \downarrow \rangle \), we neglect this effect in this section, which is appropriate when \( \lambda \) is small and the vibration coordinate is well-separated from the crossing point of the diabatic potential surfaces. The values of the parameter is sensitive to the overall behavior of the system, and we consider the conditions presented below to make a physically appropriate discussion, i.e., the “true” ground state is of the Hamiltonian (1) is basically given by

\[ |g\rangle = | \downarrow 0 \rangle_{\vec{r}_1} \otimes | \downarrow 0 \rangle_{\vec{r}_2} \otimes | \downarrow 0 \rangle_{\vec{r}_3} \otimes \ldots, \]

where

\[ |\eta nm\rangle \equiv |\eta\rangle_{\vec{r}} \otimes |n\rangle_{\vec{r}} \quad (\eta = \uparrow, \downarrow), \]

and the energy expectation value is \( \sim 0 \). This condition requires the values of the parameters to satisfy the following formulae according as the sign of \( \alpha \).

(i) \( \alpha > 0 \)
(a) Electronic excitation of any single site does not have negative value of the energy. Thus we have a condition
\[ \varepsilon > 0. \] (4)

(b) Electronic excitation of any pair of neighboring sites costs finite energy. This condition requires the value of the Coulomb interaction parameter \( V \) to be
\[ V < \frac{2\hbar\omega}{N} \left( \varepsilon + \frac{\alpha s^2}{1 + N\alpha} \right). \] (5)
where \( N \) denotes the number of nearest neighbor cells.

(c) Since the lowest energy vibration mode is realized as alternating deformation of the whole lattice, we divide the two-dimensional square lattice into two sublattices. Then one of the candidates for the low-lying many-body excited states is composed of \( | \downarrow \rangle_{\vec{r}} \) on all the sites belonging to one of the sublattices, \( | \uparrow \rangle_{\vec{r}} \) on all the sites belonging to the other, and the lowest vibration mode. Requiring the energy of this to be larger than 0, we obtain another condition
\[ \alpha < \frac{1}{N}, \] (6)
and
\[ \varepsilon > \frac{N^2 s^2 \alpha^2}{1 - N^2 \alpha^2}. \] (7)

(ii) \( \alpha < 0 \)

(a) Energy of a single electronic excitation is larger than 0, and hence
\[ \varepsilon > 0. \] (8)

(b) Contrary to (i)-(c), the low-lying many-body state we should consider is composed of \( | \uparrow \rangle_{\vec{r}} \) on every site and the lowest energy vibration mode which is identical to uniform deformation of the lattice. Then we derive other conditions
\[ \alpha > -\frac{1}{N}, \] (9)
and
\[ V < \frac{2\hbar\omega}{N} \left( \varepsilon + \frac{\alpha s^2}{1 + N\alpha} \right). \] (10)

In particular equations (6) and (9) are important in higher dimensional systems, i.e., the maximum value of \( |\alpha| \) is smaller as the dimensionality of the systems is higher.

As for the method of calculation, we numerically solved the Schrödinger equation
\[ i\hbar \frac{\partial |\Phi(t)\rangle}{\partial t} = \mathcal{H} |\Phi(t)\rangle, \] (11)
with the initial condition
\[ |\Phi(0)\rangle = | \downarrow \rangle_{\vec{r}} \otimes | \downarrow \rangle_{\vec{r}_2} \otimes | \downarrow \rangle_{\vec{r}_3} \otimes \cdots | \uparrow \rangle_{\vec{R}} \otimes \cdots | \downarrow \rangle_{\vec{r}_{N-2}} \otimes | \downarrow \rangle_{\vec{r}_{N-1}} \otimes | \downarrow \rangle_{\vec{r}_N}. \] (12)

As for the calculation method, we neglect the correlation of the fluctuation between neighboring cells, which contributes to the intersite interaction in equation (1), i.e., the inter-cell interaction \( \alpha \) and \( V \) as “mean-field”, where the influence of the neighboring cells is substituted by the expectation values. This approximation has an advantage in dealing with large systems by numerical calculation, and hence we calculated the systems with up to \( 128 \times 128 \) cells with periodic boundary condition.
3. Calculated Results

We calculated various cases for the values of the parameters discussed in the last section. We found that any excited state domain does not grow when \( \alpha < 0 \). This is an essential difference to the previous study with a one-dimensional chain[8], where \( \alpha \) takes sufficiently large value. Hence, in two-dimensional cases the interplay of the dispersion of the lattice vibration and the Coulomb interaction between electrons is necessary to drive the growth of an excited-state domain.

Figure 1. Population of \( |↑⟩_r \) for (a) \( t = 0 \), (b) \( t = 6 \), (c) \( t = 12 \), and (d) \( t = 18 \). The values of the parameters are: \( \omega = 1 \), \( s = 2 \), \( ε = 5.2 \), \( λ = 1 \), \( α = -0.1875 \), and \( V = 3.45 \).

Figures 1-(a)-(d) show the population of excited electronic state \( |↑⟩_r \) as a function of time \( t \). The values of the parameters are: \( \omega = 1 \), \( s = 2 \), \( ε = 5.2 \), \( λ = 1 \), \( α = -0.1875 \), and \( V = 3.45 \). An initially excited state is placed at the center of the lattice in the figures. We found that the conversion from \( |↓⟩_r \) to \( |↑⟩_r \) proceeds as \( t \) increases in this case and an excited-state domain grows around the initially excited cell.

Since the dispersion of the vibration mode for \( α > 0 \) does not favor the deformation of neighboring sites in the same direction, it interrupts the growth of a domain composed of \( |↑⟩_r \). However, when \( V \) is sufficiently large, the energy gain by the Coulomb interaction overcomes the effect of the dispersion, and hence the excited-state domain is formed and grows.

Figures 2-(a)-(d) show the deformation of lattice \( \langle Φ(t)|u_Φ|Φ(t)⟩ \) as a function of time. Comparing figures 1 and 2, we found that the lattice deformation and the population of the excited electronic state synchronously grows in the central part of the domain. However, figure 2 shows that the cells in the vicinity of the interface between two domains alternatingly deform, which shows that the vibration mode with short wavelength is excited before electronic state conversion. After excited electronic state is generated on one of the sublattices by the deformation of the lattice, the Coulomb interaction induces the conversion of the electronic states on the other sublattice, and thus the uniformly converted domain appears. Thus, although \( α \) seems to be unnecessary to the domain growth at the first sight, it contributes to a part of the elementary processes of the domain growth.
Figure 2. Deformation of lattice $\langle \Phi(t)\vert u_r\vert \Phi(t) \rangle$ for (a) $t = 0$, (b) $t = 6$, (c) $t = 12$, and (d) $t = 18$. The values of the parameters are: $\omega = 1$, $s = 2$, $\varepsilon = 5.2$, $\lambda = 1$, $\alpha = -0.1875$, and $V = 3.45$.

4. Discussion and Conclusions
We calculated the dynamics of the photoinduced domain growth triggered by a single-site excitation. We found that, the dispersion relation of the relevant vibration mode is required to be convex, i.e., the vibration mode with the lowest energy corresponds to that at the corner of the Brillouin zone. Since the vibronic coupling in this case does not favor the growth of excited-state domain by itself, we should take into account another type of interaction between molecular cells. We showed by numerical calculation that the Coulomb interaction between excited electronic states in neighboring cells is sufficient for the domain growth.

Although the interplay of different types of inter-cell interaction is important, the dispersion of the vibration mode and the Coulomb interaction affects oppositely to the conversion of the electronic state. This aspect appears in the elementary processes of the domain growth particularly the conversion between the electronic states in the vicinity of the interface between domains. In other words, the conversion takes place via three processes, i.e., alternating lattice deformation is induced at first and the excited electronic state $\vert \uparrow \rangle_r$ is favorable in the deformed cell. Then the Coulomb interaction induces the electronic transition in the cells on the other sublattice, and the deformation of the lattice becomes uniform after electronic state conversion takes place.

Although the necessary conditions including equations (4)-(10) for the realization of the domain growth is shown, we have not obtained sufficient conditions yet. This aspect as well as the understanding of the interaction between growing domains are future problems particularly in higher dimensional systems.

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