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# Multiple time scale population transfer-dynamics in coupled electronic states

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ABSTRACT

We regard the wave-packet dynamics in two electronic states which interact via a constant coupling element. Performing numerical calculations it is found that the time-dependent populations exhibit oscillatory variations with two characteristic periods. Whereas, as expected, one period is determined by the vibrational motion, it is shown that Rabi-type oscillations occur which are influenced by the parameters of the potential energy curves, the coupling and the amplitudes in the two states on one hand, and by the nuclear motion on the other. An analysis of the numerical results is performed within various levels of approximation.



## 1. Introduction

The preparation of quantum wave packets and the detection of their motion in real time is at the heart of Femtochemistry [1]. Femtosecond laser pulses possess a spectral width which allows to prepare coherent superpositions of ro-vibrational molecular eigenstates. Because in molecules the density of electronic states increases with excitation energy, it is usually found that the energy gap between electronic states becomes comparable to that between vibrational states in excited states. As a consequence, the interaction with ultra-short laser pulses then prepares a superposition of vibronic states, i.e. nuclear wave packets belonging to different electronic states which are coupled non-adiabatically.

Coupled electron-nuclei dynamics was investigated in the pioneering studies of Zewail and co-workers in experiments on alkali halides and, in particular, on the NaI molecule [2–7]. Adopting a diabatic picture [8] where the potential curves of two states cross but are coupled via a potential matrix element, the laser induced dynamics in NaI proceeds in a dissociative state which is coupled to a bound state. This gives rise to the predissociation dynamics where successively fractions of the initially prepared wave packet, which performs a quasi-bound motion, enter into the dissociation channel producing atomic fragments Na and I [9–16]. Within an adiabatic picture, the potentials of the two electronic states exhibit an avoided crossing which is a typical behavior in diatomic alkali halides [17]. If more than one vibrational degree of freedom is involved, electron-nuclei coupling gives rise to the phenomenon of a conical intersection [18–20] which causes a complicated vibronic dynamics [21,22].

In the present work we first investigate a restricted model in a single nuclear degree of freedom ($x$) and two electronic states. The potential curves (diabatic and adiabatic) are shown in Fig. 1. Such curves are commonly used to describe electron [23] or, in general, charge-transfer processes taking place along a reaction coordinate [24]. In fact, the parameters used in setting up the potentials are taken from former studies on the charge transfer properties of mixed valence compounds [25,26]. The scenario evolving from the picture in Fig. 1 is as follows. Starting in a 'symmetry broken state', i.e., in the local configuration where the wave function is localized in the potential well of $V_1^d$, an excitation promotes this wave function into the second electronic state with potential $V_2^d$. Afterwards, a wave-packet motion takes place where, due to the coupling, population is transferred between the two electronic states. This, eventually, leads to a periodic exchange of population (if relaxation processes are neglected) where the time scale for the exchange is determined by the nuclear wave-packet dynamics.

In this paper, we show that besides the expected time-dependence of the populations in the electronic states a second kind of oscillations can be seen which are related to Rabi-oscillations as discussed in the case of strong field laser-excitations [27]. These oscillations are highly sensitive to various parameters of the system and, in particular, are influenced critically by the nuclear wave-packet dynamics. In Section 2 we define the single-mode model used to describe the vibronic wave-packet dynamics and also its extension to several degrees of freedom. The results are presented in Section 3 which also contains a short conclusion.

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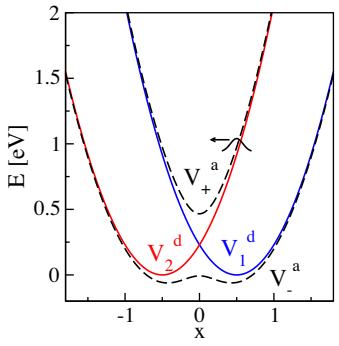


**Fig. 1.** Diabatic potentials $V_n^d(x)$ and adiabatic potentials $V_\pm^a(x)$ for a coupling of $J = 0.237$ eV and re-organization energy $\lambda = 0.917$ eV. For the propagation, a Gaussian wave packet is placed in the diabatic state $|2\rangle$ whereas state $|1\rangle$ is not populated initially.

## 2. Model

Taking only a single degree of freedom into account, we employ a Hamiltonian with two electronic states $|1\rangle$ and $|2\rangle$ as:

$$\hat{H}^d(x) = \sum_{n=1}^{2} |n\rangle\, H_n^d(x)\, \langle n| + |1\rangle\, J\, \langle 2| + |2\rangle\, J\, \langle 1|, \tag{1}$$

with the vibrational Hamiltonians:

$$H_n^d(x) = -\frac{1}{2m^*}\frac{d^2}{dx^2} + \lambda(x - x_n)^2. \tag{2}$$

Here, $x$ is a dimensionless coordinate for the vibrational degree of freedom, and the effective mass is taken as $m^* = 1005\ \text{eV}^{-1}$ [26]. The equilibrium distances of the two shifted harmonic oscillators are $x_1 = 0.5$ and $x_2 = -0.5$, respectively. The oscillators are coupled by a constant coupling element $J$. We choose a value of $\lambda = 0.917$ eV (reorganization energy), and the coupling is fixed to a value of $J = 0.237$ eV.

The potentials $V_n^d(x)$ of the two diabatic states are shifted harmonic oscillator curves and are displayed in Fig. 1. Also shown are the adiabatic potentials $V_\pm^a(x)$ obtained by diagonalization of the diabatic potential matrix:

$$V_\pm^a(x) = \frac{V_1^d(x) + V_2^d(x)}{2} \pm \frac{1}{2}\sqrt{\left(V_2^d(x) - V_1^d(x)\right)^2 + 4J^2}. \tag{3}$$

The diabatic potentials cross at the point $x_c = 0$. For the chosen coupling, the adiabatic potentials are well separated.

Given an initial (diabatic) wave function $\underline{\psi}^d(x, t = 0)$, we numerically solve the time-dependent Schrödinger equation [28]:

$$i\frac{\partial}{\partial t}\begin{pmatrix}\psi_1^d(x,t)\\ \psi_2^d(x,t)\end{pmatrix} = \left[-\frac{1}{2m^*}\frac{d^2}{dx^2}\,\mathbf{1} + \begin{pmatrix}V_1^d(x) & J\\ J & V_2^d(x)\end{pmatrix}\right]\begin{pmatrix}\psi_1^d(x,t)\\ \psi_2^d(x,t)\end{pmatrix}, \tag{4}$$

where $\mathbf{1}$ is the unit matrix. This yields the time-dependent two-component wave function from which we calculate the populations ($n$ = 1,2):

$$P_n(t) = \int_{-\infty}^{\infty} dx\, |\psi_n^d(x,t)|^2 = \int_{-\infty}^{\infty} dx\, \rho_n^d(x,t), \tag{5}$$

where $\rho_n^d(x,t)$ denotes the probability density in state $|n\rangle$.

Below, we also regard the 'adiabatic' wave functions which are obtained as

$$\underline{\psi}^a(x,t) = \hat{D}^{-1}\left(\underline{\psi}^d(x,t)\right)^\dagger = \left(\psi_+^a(x,t), \psi_-^a(x,t)\right), \tag{6}$$

where $\hat{D}^{-1}$ is the inverse of the matrix $\hat{D}$ which diagonalizes the diabatic potential matrix.

To investigate if the effects found in the single-mode model are still present in a more complex situation, we extend the description and include more vibrational degrees of freedom. The time-propagation is performed with the Multi Configuration Time Dependent Hartree (MCTDH) method [29,30], using the Heidelberg program-package [31]. As vibrational (diabatic) Hamiltonian in state $|n\rangle$ we choose

$$H_n^d = \sum_{i=1}^{N}\left(-\frac{1}{2m^*}\frac{\partial^2}{\partial x_i^2} + \frac{m^*}{2}\omega_i^2(x_i - x_{n0})^2\right), \tag{7}$$

where $N$ is the number of vibrational degrees of freedom. We employ two different parameter sets with $N = 3$ and values of the vibrational frequencies of (a) $\omega_1 = 0.06$ eV, $\omega_2 = 0.05$ eV, $\omega_3 = 0.03$ eV, and (b) $\omega_1 = 0.1262$ eV, $\omega_2 = 0.1178$ eV, $\omega_3 = 0.0740$ eV, respectively. The parameter set (a) is chosen to be within the range of the parameters used in the single-mode model whereas the set (b) is taken from Ref. [32]. In addition, five-dimensional calculations with the parameter set (b) and the additional frequencies $\omega_4 = 0.1060$ eV and $\omega_5 = 0.1032$ eV are performed. The mass is set to one and the displacements $x_{n0}$ are adjusted such that the energetic distance at the initial position of the wave packet is kept fixed at a value of $\lambda = 1.1725$ eV in all cases. Fixing the equilibrium distances in state $|1\rangle$ to $x_{10}$ = 0, this leads to values of (a) $x_{20} = 18.303\ \text{eV}^{-1/2}$, ((b), $N$ = 3) $x_{20} = 8.153\ \text{eV}^{-1/2}$, and ((b), $N$ = 5) $x_{20} = 6.5177\ \text{eV}^{-1/2}$, respectively. The coupling is set to $J = 0.25$ eV.

## 3. Results

We start with the single-mode model and an initial wave function $\underline{\psi}^d(x, 0) = (0, \varphi_{10}^d(x))$, where $\varphi_{10}^d(x)$ is the ground-state harmonic oscillator wave function in state $|1\rangle$. Thus, state $|1\rangle$ is not populated initially. This, not surprisingly, changes as a function of time which can be taken from the population dynamics illustrated in Fig. 2, panel (a). It is seen that oscillations with different periodicities are present: a periodic population transfer occurs with a period of $T_v \approx 66$ fs, and faster oscillations with a period of $T_R \approx 4$ fs are found at early times ($t < 10$ fs) and after the period at $t = T_v$.

To analyze the time-dependence of the populations we regard the wave-packet dynamics in the system. In Fig. 3, the density dynamics taking place within the first 100 fs is illustrated. Shown are the densities obtained from the diabatic (left hand panels) and

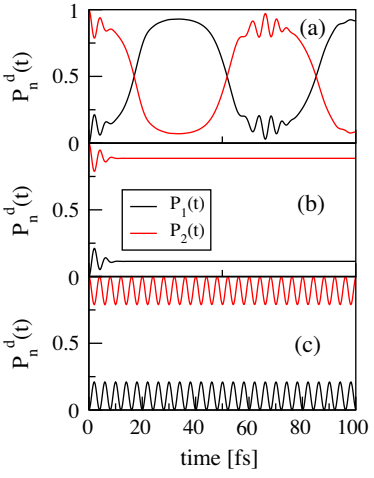


**Fig. 2.** Population dynamics in the two diabatic states, as indicated. The populations for the complete vibronic motion is displayed in panel (a). The curves in panel (b) are obtained if the kinetic energy operators in the propagators are neglected, and the dynamics for a two-level system is shown in panel (c).