Optical control of a spin switch in the weak spin-orbit coupling limit

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A method to optically control a dark transition, for instance, the coupling between different spin states, is proposed. The control is achieved by manipulating the direction, amplitude, and duration of dynamic Stark shifts. Laser-driven spin switches can be prepared by conveniently generalizing different optical techniques, such as π-pulse schemes and adiabatic passage schemes. The efficiency and robustness of the schemes is analyzed for both two-level and multilevel systems, implying quantum state selective wave packet transfer between states of different multiplicity.

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I. INTRODUCTION

In common molecular electronic structure calculations one uses the Born-Oppenheimer approach, not including the spin-orbit (SO) coupling or internal conversion terms at conical intersections in the electronic Hamiltonian. This is the standard procedure when the initial basis is not fully adiabatic [1]. The SO couplings and internal conversion terms appear as nondiagonal terms in the Hamiltonian that are usually treated as perturbations. The evolution of a quantum system in the presence of the SO couplings can be analyzed in the same way as under dipole-coupling external excitation, except that it is not possible to directly control the dynamics. In this paper we show that the control can be achieved indirectly, by manipulating nonresonant dynamic Stark shifts, which are second order field effects.

Quantum control by dynamic or dc Stark shifts has been previously proposed in various contexts. The Stark shifts induced by strong fields have been used for shaping light-induced molecular potentials, as in laser-induced bond softening or hardening [2], selectively driving population to excited states [3], changing the molecular structure [4], squeezing wave packets [5], and even influencing the outcome of photodissociation reactions at conical intersections [6] or stopping a strong spin-orbit coupling [7]. These studies analyzed the effects of Stark shifts induced by strong fields on the molecular potentials, following the dynamics in the position representation.

The effects of the couplings on the dynamics can be followed more naturally in the energy-level representation in the weak field regime. In this regime, Stark-shift control is at the core of different chirping techniques both with cw fields [8] and nanosecond pulses [9]. Additionally, coherent control techniques have also been applied to maximize the yield of dissociation reactions with spin-orbit crossings [10]. In this work we employ the dynamic Stark shift to control the population dynamics induced by "uncontrollable" dipole-forbidden intra (or inter) system couplings. As an illustration, we apply the method to the spin-orbit transition, but the validity of the results is more general.

The SO coupling has significant implications in the spectroscopy and predissociation of molecules [11,12], and in the rate of relaxation mechanisms [13]. More importantly for our study, it has immediate use in solid or molecular magnetism. The implementation of efficient and fast optical spin switches, with potential applications in molecular (or solid or surface state) memories, for example, would imply a technological breakthrough in the field of quantum information [14]. Until now, only a few schemes have been proposed using strong laser pulses. Most notably, Hübner *et al.* have proposed and numerically tested the possibility of inducing full optical spin switches by ultrashort π pulses [15], while Korolkov and Manz have used coherent control techniques to achieve the same goals [16].

In this work the target is the preparation of spin switches by Stark-shift control. The principles of the scheme can be illustrated in the following simple example. Consider a two-level system with spin-orbit coupling V_{SO}, and energy difference or splitting δ_{SO}. The spin-orbit coupling can be considered a weak perturbation as long as $\lambda = |V_{SO}/\delta_{SO}| \ll 1$. The energy of the levels can be manipulated by Stark shift so that $\delta_{SO}[\mathcal{E}(t)]$ becomes a function of the field. By a proper choice of the laser field one can reduce the splitting or even shift both levels into resonance, thus artificially making $\lambda[\mathcal{E}(t)] \gg 1$. Then, as long as the interaction is coherent and the energy splitting does not suffer from incoherent fast oscillations, the population can flow from one level to the other. Controlling the time duration and amplitude of the Stark shift one can maximize the transition probability. In this work we propose several schemes to implement efficient population switches between singlet levels to triplet levels. On the other hand, the same principles can be applied to attenuate the spin-orbit perturbation. When $\lambda \gg 1$, one must choose a field such that by Stark shift the splitting increases, making $\delta_{SO}[\mathcal{E}(t)] \gg V_{SO}$ and $\lambda[\mathcal{E}(t)] \ll 1$.

The organization of the paper is the following. In Sec. II we develop the Hamiltonian with second-order field effects. In Sec. III we propose two strategies for inducing a spin switch in a two-level system, which apply the principles of Rabi flopping and adiabatic passage, respectively. In Sec. IV we extend the results for wave packet population transfer using both schemes. Finally, Sec. V is the conclusions.

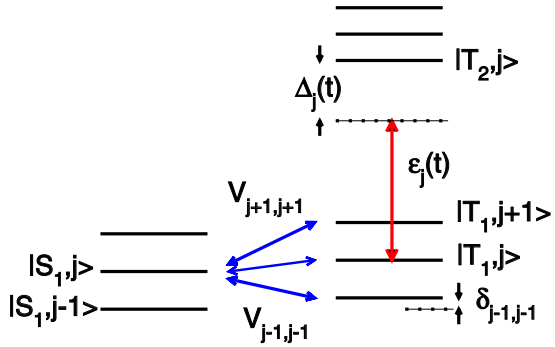

FIG. 1. (Color online) Simplified sketch of the energy level scheme of the system used for the spin switch problem.

II. MOLECULAR MODEL

In this section we derive the Hamiltonian of a quantum system with uncontrolled molecular couplings under nonresonant pulse excitation. To be specific, we consider three electronic states: the excited singlet $|S_1\rangle$, the energetically close triplet $|T_1\rangle$, and a further excited triplet $|T_2\rangle$. The first two are coupled via spin-orbit interaction, V_{SO}, while the last two are coupled via dipole moment, μ, using the fields $\mathcal{E}_j(t)$. Although more electronic states can be included in the model, the previous ones provide a minimal number needed for controlling the singlet-triplet transition. In general, a three electronic states model is sufficient to give a good description of the dynamics for most molecular systems under moderately weak fields.

In the energy representation, the system wave function can be expanded as

$$|\Psi(t)\rangle = \sum_j a_j(t)|S_1,j\rangle + \sum_j b_j(t)|T_1,j\rangle + \sum_j c_j(t)e^{-i\omega_j^{(l)}t}|T_2,j\rangle, \tag{1}$$

where the second quantum number is a collective label for the nuclear wave function and $a_j(t)$, $b_j(t)$, $c_j(t)$ are the probability amplitudes associated with state j. We can typically assign j to vibrational or rovibrational quanta of a molecule (in fact, to any degree of freedom other than spin). The notation used here is conventional. The only important point to notice is that the active levels in the quantum system involve a set of states that can be coupled by Raman processes (those sharing the first label), a set of states that can be coupled directly by dipole moment (all the $|T_1,j\rangle$ with all the $|T_2,j\rangle$ states) and a set of states that are coupled via a dark or dipole-forbidden transition (all the $|S_1,j\rangle$ with all the $|T_1,j\rangle$). A qualitative picture of the energy states of a possible spin-switch system for $j=1,\ldots,3$ is shown in Fig. 1. The phase of the excited triplets in Eq. (1) is defined by the laser frequency, $\omega_j^{(l)}$, not by the level energy, $\omega_j^{T_2}$. When more than one laser is used, the chosen phase corresponds to the frequency tuned to that transition (or closer to resonance, since the excitation will be nonresonant). Expanding the field as a sum of laser pulses of frequency $\omega_n^{(l)}$ and envelope $\mathcal{E}_n(t)$, the time-dependent Schrödinger equation (TDSE) for the system is ($\hbar=1$)

$$i\dot{a}_j = \omega_j^{S_1}a_j - \sum_k V_{jk}b_k, \tag{2}$$

$$i\dot{b}_j = \omega_j^{T_1}b_j - \sum_k V_{kj}a_k - \sum_k \mu_{jk}\left(\sum_n \mathcal{E}_n(t)\cos(\omega_n^{(l)}t)\right)e^{-i\omega_k^{(l)}t}c_k, \tag{3}$$

$$i\dot{c}_j = (\omega_j^{T_2} - \omega_j^{(l)})c_j - \sum_k \mu_{jk}\left(\sum_n \mathcal{E}_n(t)\cos(\omega_n^{(l)}t)\right)e^{i\omega_j^{(l)}t}b_k, \tag{4}$$

where $V_{jk}=\langle S_1,j|V_{\mathrm{SO}}|T_1,k\rangle$, which can always be chosen real. We have neglected the SO coupling between the $|T_2,j\rangle$ states and $|S_1,j\rangle$ states, which are very off resonant (see Fig. 1). The rotating wave approximation is now applied by making

$$\sum_n \mathcal{E}_n(t)\cos(\omega_n^{(l)}t)e^{\pm i\omega_j^{(l)}t} \approx \frac{1}{2}\sum_n \mathcal{E}_n(t)e^{\pm i\Delta\omega_{jn}^{(l)}t}, \tag{5}$$

where $\Delta\omega_{jn}^{(l)}=\omega_j^{(l)}-\omega_n^{(l)}$ (the phase difference is obviously zero for $n=j$). If $\Delta_j(t)\equiv\omega_j^{T_2}-\omega_j^{(l)}(t)>\mu_{jk}\Sigma_n\mathcal{E}_n/2$ for all $|T_2,j\rangle$ to $|T_1,k\rangle$ transitions, the nonresonant interaction can be treated by adiabatic elimination of the probability amplitudes c_j. Since the laser frequency can be chirped, in general $\Delta_k(t)$ is time dependent and the criteria for adiabatic elimination must hold for all the pulse bandwidth. Assuming that this is the case, and making $\dot{c}_j\approx 0$, one obtains

$$c_j \approx \sum_k \frac{\mu_{jk}}{2\Delta_j(t)}\sum_n \mathcal{E}_n(t)e^{i\Delta\omega_{jn}^{(l)}t}. \tag{6}$$

In Eq. (6) we do not neglect the phase oscillations due to the detuning of the different carrier frequencies. This is important only if $\Delta\omega_{j,j\pm1}\sim\Delta\omega_{jn}^{(l)}\ll\Delta_j(t)$; the opposite case $[\Delta\omega_{j,j\pm1}\gg\Delta_j(t)]$ implies an expression similar to Eq. (6) where a single pulse, $\mathcal{E}_j(t)$, replaces the sum over all the pulses.

Inserting Eq. (6) into Eq. (3) we find

$$i\dot{b}_j = \omega_j^{T_1}b_j - \sum_k V_{kj}a_k - \sum_{k,l}\frac{\mu_{jk}\mu_{kl}}{4\Delta_k(t)}\sum_{n,m}\mathcal{E}_n(t)\mathcal{E}_m(t)e^{i(\Delta\omega_{jn}^{(l)}+\Delta\omega_{mj}^{(l)})t} \tag{7}$$

from where, separating the diagonal ($m=n$) from the cross interference terms, we finally obtain

$$i\dot{b}_j = \omega_j^{T_1}b_j - \sum_k V_{kj}a_k - \sum_{k,l}\frac{\mu_{jk}\mu_{kl}}{4\Delta_k(t)}\left(\sum_n \mathcal{E}_n^2(t) + 2\sum_{n>m}\mathcal{E}_n(t)\mathcal{E}_m(t)\cos(\Delta\omega_{nm}^{(l)}t)\right)b_l. \tag{8}$$

It is interesting to observe that in Eq. (8) all pulses act on all transitions, which restricts some possible quantum interference effects. This is a consequence of assuming $\Delta\omega_{j,j\pm1}\ll\Delta_j(t)$. To further simplify the equations we use an average detuning, that is, we consider the average effect of the excited states. Thus we define the two-photon effective Rabi frequency

$$\Omega_{jk}(t) = \frac{\alpha_{jk}\mathcal{E}^2(t)}{2\Delta(t)}, \tag{9}$$

where α_{jk} is related to the polarizability matrix element, $\Delta(t)$ is the average detuning and $\mathcal{E}(t)$ is the sum of all field amplitudes. In this work we use a single pulse or a sequence of nonoverlapping pulses so that the optical interference term is zero. Therefore, only one pulse intervenes in all transitions at each instant of time.

Alternatively, we could consider the opposite limit of $\Delta\omega_{j,j\pm1} \gg \Delta_j(t)$. Since $\Delta_j(t)$ is also greater than the laser couplings, the Raman couplings could be neglected. Then Eq. (9) could still be applied for the diagonal elements, $\Omega_{jj}(t)$, where $\mathcal{E}(t)$ would be just a single laser, $\mathcal{E}_j(t)$, and $\Delta_j(t)$ (defined for each nonresonant laser transition) would replace Δ. Making these adjustments, the approximate formulas that will be developed in Secs. III and IV for the pulse schemes will be valid in both limits. For the numerical results we shall assume the first case $[\Delta\omega_{j,j\pm1} \ll \Delta_j(t)]$, which involves more undesired couplings and therefore poses more demanding conditions for the efficiency of the spin switch.

To further simplify the equations we shall also omit all SO coupling terms except for the nearest states in the singlet and triplet manifolds ($V_{jk}=0$ for $j \neq k$). This assumption can be easily removed, but it will always be satisfied for all the energy-level schemes explored in this work, in which the energy difference between $|S_1,j\rangle$ and $|T_1,j\rangle$ (δ_{jj}), must be much larger than V_{jj}. Then the TDSE is

$$i\dot{a}_j = \omega_j^{S_1} a_j - V_{jj} b_j,$$

$$i\dot{b}_j = [\omega_j^{T_1} - \Omega_{jj}(t)/2]b_j - \sum_{k\neq j} \Omega_{jk}(t) b_k/2 - V_{jj} a_j, \tag{10}$$

where the first term in the equation for b_j includes the Stark-shift effect, the second term includes the possible Raman couplings, and the last term includes the spin-orbit coupling. For pulse parameters such that $\Omega_{jk} \ll \Delta\omega_{jk}$, one can neglect the Raman transitions. In the following section we will see that Ω_{jj} must be of the order of the energy difference between the singlet and triplet levels coupled by V_{jj}, so that the previous condition will not be always satisfied and, in general, we will not neglect the Raman couplings. In this work the pulses are parametrized as $\mathcal{E}(t)=\mathcal{E}_0 \sin^2(\pi\Delta t/2\tau_1)$ for the switch on period $t \leq \tau_1$; $\mathcal{E}(t)=\mathcal{E}_0$ during the plateau region $\tau_1 < t \leq \tau_1+\tau_2$; and $\mathcal{E}(t)=\mathcal{E}_0 \cos^2(\pi\Delta t/2\tau_3)$ during the switch off period $\tau_2 < t \leq \tau_2+\tau_3$, where $\mathcal{E}_0$ is the peak (or plateau) field amplitude.

In the following we analyze two particular models. In the first one we consider population transfer from a single singlet level $|S_1,1\rangle$ to a single triplet level $|T_1,1\rangle$. We assume that the pulse parameters can be chosen so that all Raman transitions can be neglected and only those two levels participate in the dynamics, which depends on a simple effective two-level Hamiltonian. In the second model we consider population transfer from singlet to triplet superposition states. We assume all polarizability matrix elements equal to one.

III. SPIN SWITCH IN THE TWO-LEVEL SYSTEM

Following Eq. (10), the effective Hamiltonian including the SO coupling of $|S,1\rangle$ with $|T,1\rangle$ and the Stark shift induced by a nonresonant field acting on the transition between the triplet states, has the form

$$\mathsf{H} = \begin{pmatrix} 0 & V_{11} \\ V_{11} & \delta_{11} - \Omega_{11}(t)/2 \end{pmatrix}, \tag{11}$$

where $\delta_{11}=\omega_1^{T_1}-\omega_1^{S_1}$. The effective Rabi frequency acts on the diagonal terms and thus, it can only enhance the coupling by inducing the energy resonance between $|S_1,1\rangle$ and $|T_1,1\rangle$. Alternatively, it can also reduce the coupling by moving the states more out of resonance. In the limit of weak coupling, $\lambda=|V_{11}/\delta_{11}| \ll 1$, only the first case requires laser control. In addition, a second laser could be used on the transition between the singlet states, so that the Stark-shift effect could be split between both fields.

There are two simple ways of affecting the singlet-triplet transition: controlling $\mathcal{E}(t)$ and controlling $\Delta(t)$, which are related to the π-pulse scheme and the adiabatic passage scheme, respectively.

A. π-pulse scheme

In order to have an efficient population transfer between $|S_1,1\rangle$ and $|T_1,1\rangle$, one must adjust the Stark shift so that both levels are in resonance. If the resonance is maintained during the time

$$\tau = \frac{\pi}{2|V_{11}|}, \tag{12}$$

then all the population is transferred to the $|T_1,1\rangle$ state according to the Rabi formula [17]. The resonance, $\Omega_{11}=2\delta_{11}$, can be achieved by applying a constant field of amplitude

$$\mathcal{E}_0 = \sqrt{4\delta_{11}\Delta/\alpha_{11}}. \tag{13}$$

Notice that the spin switch duration is only controlled by the molecular coupling V_{11}. The pulse must be basically a constant field with fast switch on and switch off.

B. The adiabatic passage scheme

Adiabatic passage transfer is possible if we induce a chirp in $\Omega_{11}(t)$. This can be done in two ways, by approximately linearly increasing or decreasing the amplitude $\mathcal{E}(t)$, or the detuning $\Delta(t)$ via the laser frequency. Since frequency chirping is a widely extended optical technique, we first consider an adiabatic singlet-triplet crossing induced by pulse chirping. In Sec. IV C we will present some results of transform-limited pulses where the pulse amplitude is shaped so that the effective Rabi frequency changes in time, sweeping the resonance and inducing the crossing. Other pulse shapes can also induce the same overall effect.

Using a linear chirp, $\Delta=\Delta_0+\beta\Delta t/2$ (with temporal chirp β) we find that

$$\Omega_{11} = \frac{\alpha_{11}\mathcal{E}_0^2}{2(\Delta_0+\beta\Delta t/2)} \approx \frac{\alpha_{11}\mathcal{E}_0^2}{2\Delta_0}\left(1 - \frac{\beta}{2\Delta_0}\Delta t\right).$$

In Landau-Zener theory [17] the difference between the diagonal elements of the Hamiltonian is $H_{22}-H_{11}=\delta+\beta\Delta t/2$, so that the diabatic energies linearly cross each other at a certain time. By defining $\delta_{\text{eff}}=\delta_{11}-\alpha_{11}\mathcal{E}_0^2/4\Delta_0$ and

$$\beta_{\text{eff}}=-\frac{\alpha_{11}\beta}{4}\left(\frac{\mathcal{E}_0}{\Delta_0}\right)^2 \tag{14}$$

we observe that the Hamiltonian in Eq. (11) is of Landau-Zener type. Thus the adiabatic passage will occur if $|\beta_{\text{eff}}| \leqslant V_{11}^2$ [17] which requires

$$|\beta| \leqslant \frac{4V_{11}^2\Delta_0^2}{|\alpha_{11}|\mathcal{E}_0^2}. \tag{15}$$

Additionally, we make the effective chirp to sweep across the resonance at $\Delta t=0$, so that $\delta_{\text{eff}}\approx 0$ and

$$\mathcal{E}_0 \sim \sqrt{4\delta_{11}\Delta_0/\alpha_{11}}. \tag{16}$$

In this case the condition for the laser amplitude is not strict. Finally, the frequency spanned by the effective chirp must be larger than V_{11}, so that the time duration of the chirped pulse τ must be approximately larger than $2V_{11}/\beta_{\text{eff}}$ or

$$\tau \gg \left|\frac{2V_{11}}{\beta_{\text{eff}}}\right| = \left|\frac{8V_{11}\Delta_0^2}{\alpha_{11}\beta\mathcal{E}_0^2}\right|. \tag{17}$$

Inserting Eq. (16) for the field amplitude onto Eqs. (15) and (17), we obtain the following "optimal" conditions for the chirp and time duration of the pulse

$$|\beta| \sim \left|\frac{\Delta_0}{\delta_{11}}\right| V_{11}^2 \tag{18}$$

and

$$\tau \gg \left|\frac{2V_{11}\Delta_0}{\beta\delta_{11}}\right| \sim \frac{1}{\gamma|V_{11}|}, \tag{19}$$

where $\gamma \ll 0.5$. Finally, in order to guarantee the adiabatic passage, special care must be taken either at the beginning (for negative chirp) or at the end (for positive chirp) of the pulse. Since the effective chirp in Eq. (11) is induced by the Rabi frequency, the chirp is always parabolic, that is, it changes sign as the pulse turns on or off, causing a double crossing with the triplet state. In order to avoid the unwanted adiabatic crossing the pulse must be either turned on or off abruptly making the corresponding crossing nonadiabatic.

The advantage of the adiabatic passage scheme over the π-pulse scheme is that γ can be varied over a reasonable range so that $\mathcal{E}_0$, β, and τ do not have to satisfy exact control conditions. This is important for multiple singlet-triplet transitions. The clear disadvantage of the adiabatic passage scheme is the need for long pulse durations which in turn require a long coherence time.

C. Numerical results

The numerical results shown here and in the following sections imply solving the time-dependent Schrödinger equation in the energy representation by the standard fourth-order Runge-Kutta scheme [18]. A practical spin switch requires $\lambda \ll 1$, since otherwise the natural spin dynamics already switches the populations in a uncontrolled way. We choose $\bar{\delta}_{11}=\delta_{11}/V_{11}=10$, which already implies a non-negligible singlet-triplet population transfer in the absence of the laser pulse, with consequences of the laser-induced population dynamics. Without loss of generality we consider $\alpha_{11}=1$.

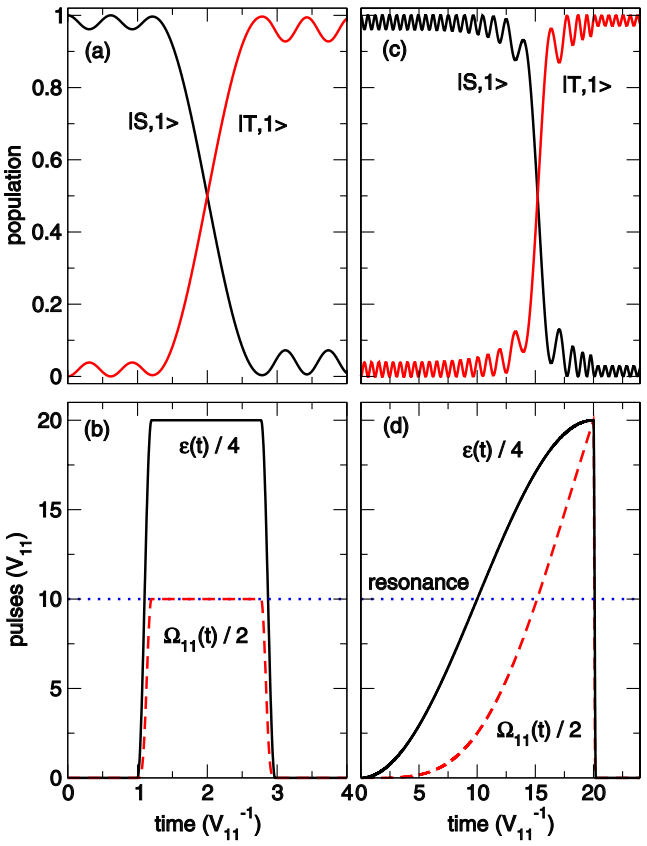

FIG. 2. (Color online) Population dynamics in the two-level spin switch using the π-pulse strategy (a) and the adiabatic passage strategy (c). The required scaled pulse amplitudes (solid line) and effective Rabi frequencies (dashed line) for the previous strategies, are shown on (b) and (d), respectively.

The results of implementing the π-pulse scheme are shown in Fig. 2(a). We use a pulse with a fast turn on and turn off and constant field amplitude [Fig. 2(b)], so that the pulse duration is approximately τ_2. The laser-induced resonant population transfer occurs during $\tau_2=\pi/2$, where the time scale is normalized by V_{11}. We choose $\tau_1=\tau_3=0.2$ and $\Delta_0=16\delta_{11}$ so that $\mathcal{E}_0=80V_{11}$. The population transfer depends weakly on the wave function phase, which is changing even in the RWA because of V_{11}. For $\bar{\delta}_{11}\gg 1$ this dependence is negligible.

The results of implementing the adiabatic strategy are shown in Fig. 2(c). We use a negatively chirped pulse and $\Delta_0=16\delta_{11}$, $\gamma=0.1$, so that following Eqs. (16), (18), and (19) we find $\mathcal{E}_0=80V_{11}$, $\beta=-16V_{11}^2$, and $\tau=10$. Given our choice of chirp sign, the system crosses the resonance from lower frequencies to higher frequencies, therefore the pulse must imply slow turn on and fast turn off stages. We use $\tau_2=0$ and $\tau_1\approx 2\tau=20$ and as before $\tau_3=0.2$. Again the results depend

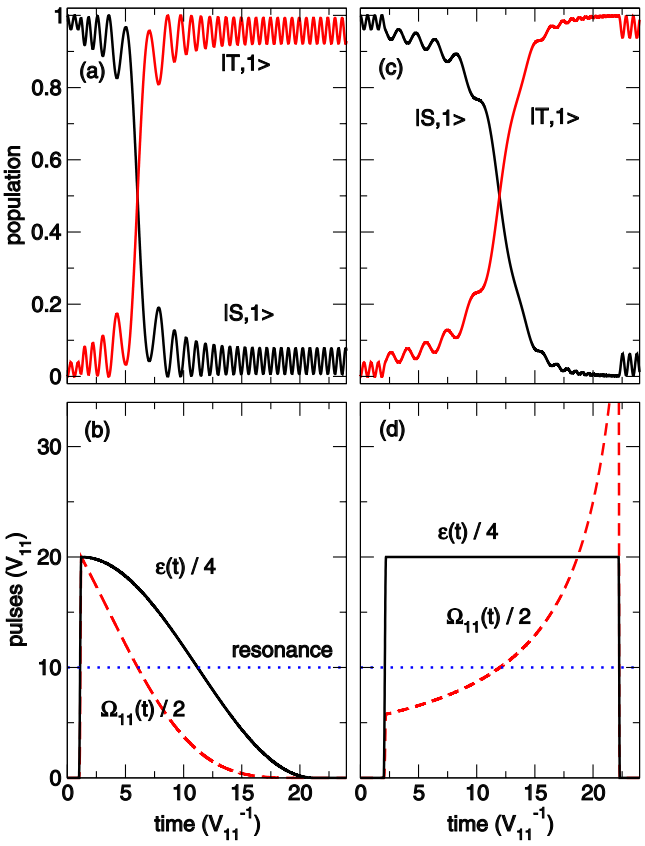

FIG. 3. (Color online) Population dynamics in the two-level spin switch using the adiabatic passage strategy with a positively chirped fast turn-on, slow turn-off pulse (a); and with a negatively chirped, constant field (c). The required pulse amplitudes (solid lines) and effective Rabi frequencies (dashed lines) are shown on (b) and (d) for both previous schemes, respectively.

on the phase of the wave function and the population transfer is relatively sensitive to the time duration and even to the turn off time.

In Landau-Zener theory the transfer occurs for infinite time and it is only sensitive to the chirp rate. For the chosen parameters, Landau-Zener predicts a yield of population transfer better than 99.8%, which could be improved by decreasing the chirp rate β. However, in the spin-orbit laser-induced adiabatic passage scheme, the initial distance from the resonance is given by δ_{11}, a fixed molecular parameter. The time duration of the transfer is finite and the final separation from the resonance depends on the shape of the laser pulse, the chirp rate and the pulse duration. The smaller β, the larger the pulse must be to assure significant population transfer. But a too small β implies considerable phase dependence of the population transfer, since at initial times the energy separation from the resonance is not large enough. Therefore, if V_{11} is not much smaller than δ_{11}, the dynamics is sensitive both to the shape and to the sign of the chirp.

In Fig. 2(d) we show the effective Rabi frequency and the position of the resonance. In Fig. 3(b) we use the same parameters but with positive chirp, $\beta=16V_{11}^2$. Now the resonance is crossed from higher frequencies to lower frequencies. Therefore we need a fast turn-on and slow turn-off pulse shape. The transfer is not so perfect since the Rabi frequency sweeps the resonance in a less efficient way. Typically the results are more sensitive to the initial wave function phase, since the laser must be turned on abruptly with positive chirp. In Figs. 3(c) and 3(d) we show results using a constant field with both fast turn-on and turn-off. We have chosen $\tau_1=\tau_3=0.2$ and $\tau_2=20\approx\tau$, so that $\gamma=0.05$ and $\beta=-24V_{11}^2$. In order to achieve excellent population transfer with constant fields we need to use longer pulses and higher chirp rates, so that the energy levels are more distant from the resonance both at the beginning and at the end of the process. Alternatively, the pulse could be asymmetrically chirped in time, such that the carrier frequency (Δ_0) is displaced to the tail of the pulse.

IV. SPIN SWITCH OF SUPERPOSITION STATES

We consider now the transfer of a singlet superposition state, that is, a wave packet of singlet states, onto the triplet manifold. Again we address the case where the laser-free SO couplings are weak among all participant levels, that is $\delta_{jj}=(\omega_j^{T_1}-\omega_j^{S_1})\ll V_{jj}$. As in the two-level system, a better transfer efficiency is achieved by manipulating the energy levels via Stark shifts. For an n-level superposition state the required Stark shifts can be induced by a single pulse or by a sequence of n pulses, each driven by a different nonresonant carrier frequency.

The model depends now on many parameters, namely the energy difference between the singlet and triplet levels or spin-orbit splittings δ_{jj}, the spin-orbit couplings V_{jj}, and the energy difference between adjacent levels on the triplet manifold, $\Delta\omega_{j,j+1}$. The role of the different parameters can be conveniently described by their statistics. We consider the average of the singlet-triplet splittings $\langle\delta\rangle$ and its standard deviation $\Delta\delta$; and the average of the spin-orbit couplings $\langle V\rangle$ and its standard deviation ΔV. These four parameters characterize the molecular system of the singlet-triplet switch. We define the variability parameter $\xi=\Delta V/|\langle V\rangle|=\Delta\delta/|\langle\delta\rangle|$ (we typically use the same variability for both parameters, although this is not necessary) to account for the statistics in a simplified way. Finally, the average energy difference between adjacent states in the triplet, $\Delta\omega$, determines the importance of the Raman transitions. In order to simplify the model we shall consider that the detuning Δ to the excited triplet states is the same for all levels and that the initial state is a linear superposition of three singlet levels with identical populations. All polarizability elements α_{ij} are taken as unity. These simplifications do not pose any fundamental constraint to the model.

A. π-pulse scheme

Depending on the parameters of the system, the π-pulse scheme can be implemented in different ways. The straightforward extension of the two-level scheme implies using a pulse sequence in which each pulse $\mathcal{E}_j(t)$ controls a single transition $|S_1,j\rangle\rightarrow|T_1,j\rangle$ with optimal parameters

$$\mathcal{E}_{0j}=\sqrt{4\delta_{jj}\Delta_j/\alpha_{jj}} \tag{20}$$

and

$$\tau_j = \frac{\pi}{2|V_{jj}|} \tag{21}$$

such that $\Omega_{jj}/2=\delta_{jj}$. The pulses could be applied at the same time or sequentially, since in principle the order of the sequence should not affect the outcome of the dynamics.

There are two problems with the sequential transfer, however. The first one is that each pulse in the sequence crosses every resonance at the switch on and switch off. Considering, for instance, that we first apply the pulse for which the splitting is the smallest (δ_{ss}), which requires the smallest pulse amplitude, the population will flow from $|S_1,s\rangle$ to $|T_1,s\rangle$. However, when we apply the next pulse to transfer the population from a different singlet level, the induced Stark shift will also operate over $|T_1,s\rangle$, crossing again the resonance. The switch on and off periods must therefore be fast enough to avoid changing the pulse area of each "independent" interaction.

The second problem is related to the previous one. If for two levels in the manifold $|\delta_{kk}-\delta_{ll}| \leqslant |V_{kk}|, |V_{ll}|$, then both $\mathcal{E}_k(t)$ and $\mathcal{E}_l(t)$ will affect both transitions. One needs $|\delta_{kk}-\delta_{ll}| \gg |V_{kk}|V_{ll}| \forall k,l$, or roughly $\Delta\delta \gg |\langle V\rangle|$, in order that the transfer of all levels is independent. This condition can be easily satisfied only for very weak couplings. With the parameters explored in this work for the two-level system, the dependence of the transfer (the area of the Rabi flopping) on the phase is even more severe in the n-level case than in the two-level system, as we show numerically.

In a different limit, the parameters of the system may be such as to allow a parallel switching. If $\Delta\delta \ll |\langle\delta\rangle|$ and $\Delta V \ll |\langle V\rangle| \ll \Delta\delta$ (assuming as well that $\Delta_{jj}\sim\Delta$ and $\alpha_{jj}\sim\alpha$ are similar for all transitions, as built in our model) then it is possible to switch the whole singlet wave packet to the triplet manifold using a single pulse with average parameters $\mathcal{E}_0=\sqrt{4\langle\delta\rangle\Delta/\alpha}$ and $\tau=\pi/2|\langle V\rangle|$ such that $\Omega_{\text{eff}}/2=\langle\delta\rangle$.

Finally, since $\Omega_{ij}\sim\Omega_{jj}\sim 2\delta_{jj}$, the Raman Rabi frequencies Ω_{jk} [Eq. (10)] will couple the different triplet levels unless $\Delta\omega \gg |\langle\delta\rangle|$. We show numerically that when the Raman couplings are important, not only the relative populations of the triplet levels may differ from those of the initial singlet wave function, but also the whole singlet-triplet transfer can be severely affected.

B. Adiabatic passage scheme

The extension of the adiabatic passage scheme to the spin switch of superposition states is straightforward. A single pulse can be used with the same parameters given by Eqs. (16), (18), and (19) substituting δ_{jj} and V_{jj} by the corresponding average values $\langle\delta\rangle$ and $\langle V\rangle$, as long as the standard deviations in the parameters (the variability ξ) are not too large. That is, $\langle\delta\rangle\pm\Delta\delta$ must fall under the envelope of the effective Rabi frequency $\Omega_{\text{eff}}(t)/2$ and γ must be small enough that

$$\tau \ll \left|\frac{2\Delta_0}{\beta}\frac{\langle V\rangle+\Delta V}{\langle\delta\rangle-\Delta\delta}\right|. \tag{22}$$

Under these conditions the wave packet can be switched to the triplet manifold by a single pulse, whose effective Rabi frequency adiabatically sweeps all δ_{jj} resonances. However, the relative populations in the triplet manifold may suffer oscillations if $\Delta\omega$ is not much larger than $|\langle\delta\rangle|$.

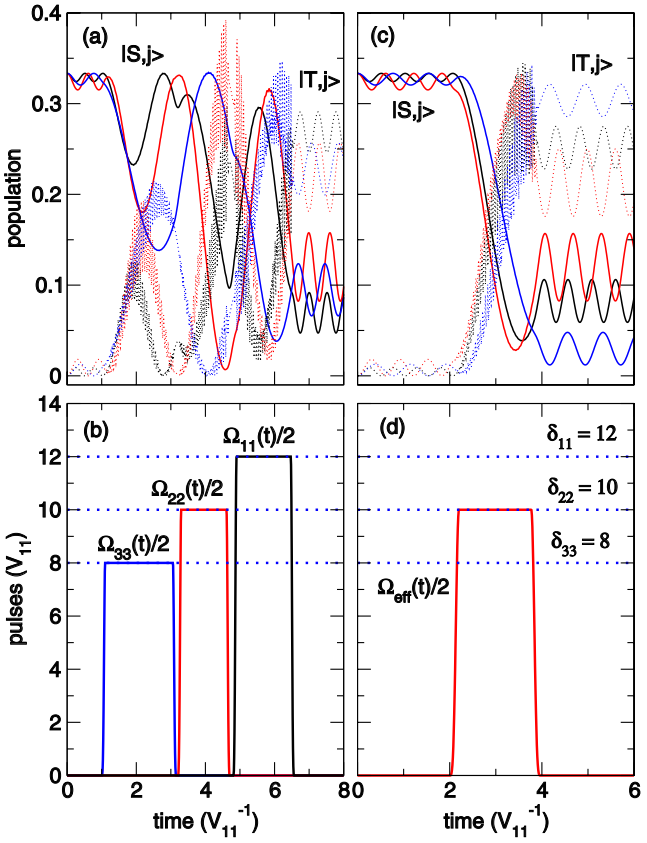

FIG. 4. (Color online) Population dynamics in the spin switch of a superposition state using the generalized π-pulse strategy with a sequence of π pulses (a) and with a single pulse with averaged parameters (c). The required pulse Rabi frequencies for the previous strategies together with the position of the different resonances are shown in (b) and (d), respectively.

C. Numerical examples

As in the two-level system we only address the weak coupling ($\lambda \ll 1$) case, choosing $\langle\delta\rangle=10\langle V\rangle$. In Fig. 4 we show the dynamics of a typical π-pulse implementation with $\xi=\Delta\delta/|\langle\delta\rangle|=\Delta V/|\langle V\rangle|=0.2$. This case implies small variability in the spin-orbit couplings and splittings, and one can implement the π-pulse strategy using both one pulse and a sequence of three pulses. In both cases we obtain a relatively good 80% overall transfer from the singlet manifold to the triplet manifold, starting with a three-level superposition with equal populations in the singlet manifold. For the dynamics shown in Fig. 4, we have chosen $\Delta\omega=10\langle\delta\rangle$, so that the vibrational spacing is 5 times the maximum Rabi frequency. The pulse parameters of the three-pulse sequence were chosen following Eqs. (20) and (21), while the parameters of the single pulse are the same as those for the two-level system, since $\langle V\rangle=V_{11}$ and $\langle\delta\rangle=\delta_{11}$. In Fig. 4 we show the individual populations of the different singlet and triplet

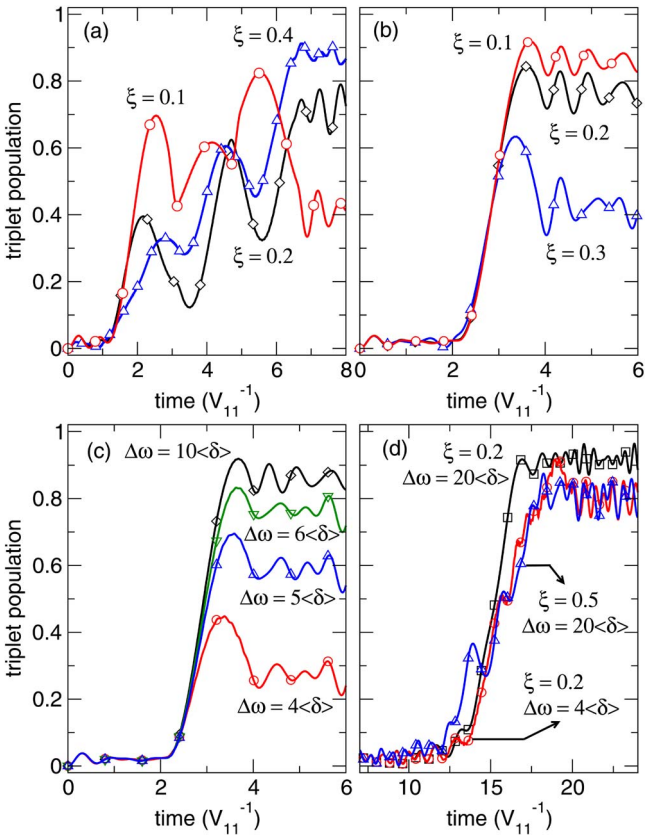

FIG. 5. (Color online) Efficiency of the overall spin switch of a superposition state. In (a) we show the effect of the system variability over the π-pulse sequence scheme; the same effect is observed over the single π-pulse strategy in (b). In (c) we show the effect of the Raman couplings over the single π-pulse scheme, and in (d) we show the effects of both Raman couplings and system variability over the adiabatic strategy. Details of the parameters are given in the text.

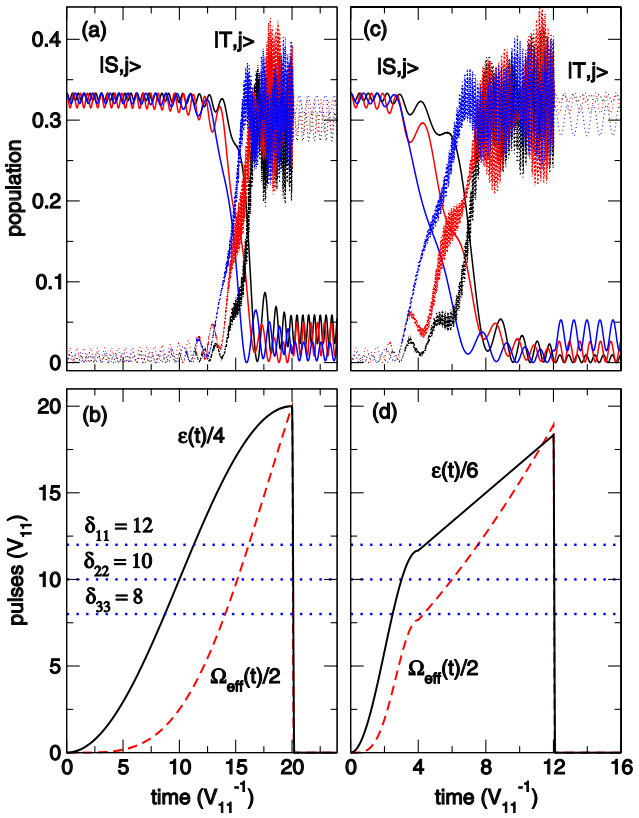

FIG. 6. (Color online) Population dynamics in the spin switch of a superposition state using the adiabatic strategy with a negatively chirped slow turn-on, fast turn-off pulse (a); and with a transform-limited pulse with linearly increasing amplitude (c). The required scaled pulse amplitudes (solid lines) and effective Rabi frequencies (dashed lines) for the previous schemes are shown in (b) and (d), respectively. The different crossed resonances are shown by dotted lines.

levels so that for each $|S,i\rangle \rightarrow |T,i\rangle$ transition a relatively high yield is achieved.

In fact, for the chosen molecular parameters the three transitions cannot be considered independent, since $\Delta\delta \sim 2\langle V\rangle$ and therefore every pulse acts on every transition, as Fig. 4(a) shows. The high efficiency of the pulse sequence is due to the accidental fact that the accumulated pulse areas for each transition are approximately π at the end of the pulse sequence. In Fig. 5(a) we show the overall population of the triplet for different variabilities in the model. Clearly, the sequential π-pulse scheme performs better as ξ increases. This is because one needs $\Delta\delta \geqslant 6\langle V\rangle$ (which in the model is obtained by choosing $\langle\delta\rangle = 14\langle V\rangle$ and therefore $\xi \sim 0.4$) for the transitions to become more independent. But even when the transitions are not independent and Eqs. (20) and (21) do not guarantee a high yield of population transfer, it is always possible to optimize the pulse amplitudes and time durations so that a high efficiency is finally achieved. That is, the sequential scheme involves enough laser parameters to control the dynamics.

On the contrary, using the single π-pulse scheme, the dynamics depends only on two laser parameters, τ and $\mathcal{E}_0$, which are insufficient to fully control the spin switch and guarantee an efficient transfer when ξ is large. In Fig. 5(b) we show how the efficiency of the singlet-triplet transfer is affected as ξ varies. The π scheme is more sensitive to large variations in $\Delta\delta$ than in ΔV. The numerical results show that using the average parameters the yield is always close to maximum, although this maximum quickly decreases with ξ.

The π-pulse scheme (both with a single pulse or a pulse sequence) is quite sensitive to the Raman couplings. Raman transitions induce significant population transfer among the triplet levels, as Figs. 4(a) and 4(c) show, and affect as well the overall efficiency of the transfer. In Fig. 5(c) we show the overall triplet population as a function of time for increasing Raman couplings ($\Delta\omega$), using the π-pulse scheme with a single pulse and ξ=0.1. The efficiency of the transfer is basically not affected until $\Delta\omega < 7\langle\delta\rangle$. For $\Delta\omega \sim 4\langle\delta\rangle$ (twice the peak effective Rabi frequency) the population remains mainly in the singlet manifold. Similar results are obtained with the sequential π-pulse scheme.

For the singlet-triplet wave packet transfer it is certainly much more efficient to use the adiabatic strategy. In Fig. 6 we show two typical examples with ξ=0.2, using either a pulse with slow switch on and fast switch off (with the same

parameters as in the two-level system, $\gamma=0.1$, in Sec. III C) or a transform-limited pulse with linear variation in the pulse amplitude, in which the plateau region is replaced by a linearly increasing field. For this field the time duration is typically close to τ_2, instead of the τ_1 for the slow switch on pulse. Other pulse shapes such that the effective Rabi frequency sweeps across the level resonances work in the same way.

For both pulses in Fig. 6 the spin switch performs with high efficiency (greater than 90%), since the effective Rabi frequency sweeps across the resonance of all the singlet-triplet transitions. The method is quite robust to large variations in the spin-orbit couplings and splittings, and the pulse parameters can vary over a broad range. In fact, the amplitude-shaped pulse is typically even more efficient, requiring smaller pulse durations.

In Fig. 5(d) we show that for $\xi=0.5$ the efficiency of the transfer is still better than 80% using the same pulse as in the two-level case. Additionally, the adiabatic passage scheme is much more robust to the effect of the Raman couplings. In Fig. 6 we use $\Delta\omega=20\langle\delta\rangle$, so that the vibrational spacing is about 5 times the maximum Rabi frequency. However, even for $\Delta\omega=4\langle\delta\rangle$ (when the vibrational spacing is approximately equal to the maximum Rabi frequency) the overall efficiency of the transfer is higher than 80%, as Fig. 5(d) shows. That is, even when all transitions interfere with each other and very significant transient population transfer among the triplet levels occurs, the overall singlet-triplet switch efficiency is not severely affected.

V. CONCLUSIONS

In this work we have proposed different ways of using transform-limited or chirped pulses to induce transitions between states of different spin, which are dipole uncoupled. The proposed scheme is a general procedure for transferring time-dependent control exerted by the field on one part of the Hamiltonian (where dipole moments are nonzero) into energy control that affects the desired region of the spectra where the dipole couplings are symmetry forbidden. In principle, it can be used to control any type of intramolecular (or even intermolecular) coupling. In this work we have designed optically induced spin switches between two levels or superposition states. The same procedure can be applied to stop a stronger coupling by breaking the close degeneracy. It is interesting to note that the sequential π-pulse scheme in principle uses enough pulse parameters to control the area of each transition. Arbitrary superpositions of singlet and triplet states, that is, mixed-spin wave packets, can thus be prepared.

The pulse requirements of the method do not meet very demanding conditions. If we consider a rather usual weak spin-orbit coupling of the order of 0.1 cm^{-1} between two quantum states separated by one or more wavelengths, then the scaled parameters used in our simulations imply using pulses of 100 ps duration with an intensity of the order of 10 MW/cm^2. For these parameters, the simplified model provides a reasonably good estimate of the molecular laser-induced spin-orbit dynamics as long as the energy spacing between the vibrational levels in the singlet and triplet electronic states is larger than 10 cm^{-1}. These conditions are satisfied by many diatomic molecules where the density of states is not very large. For the adiabatic passage scheme, a temporal chirp rate of 6.6×10^{-9} fs^{-2} would be needed, which could be easily achieved by linear chirping of a 300 fs transform-limited pulse, for example. The adiabatic scheme could also be applied to molecules with weaker state-to-state couplings requiring nanosecond pulses of MW/cm^2 intensity with harder to meet chirping conditions. Alternatively, one could apply it to molecules with stronger couplings using picosecond pulses of GW/cm^2 intensity. In this case many quantum states would participate in the dynamics, so that the estimates of the simple models herein employed would be questionable. It is however possible to extend the theory of spin-orbit control in the strong-field regime using the concept of laser-induced coupling or decoupling of molecular potentials [6,7].

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[1] There is a vast literature analyzing the role of nonadiabatic crossings in molecules, and studying the (laser-free) quantum dynamics at conical intersections, using both adiabatic and diabatic basis. See for instance, *Conical Intersections: Electronic Structure, Dynamics and Spectroscopy*, edited by W. Domcke, D. R. Yarkony, and H. Koppel (World Scientific, Singapore, 2004).

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