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Optical control of molecular switches

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TOPICAL REVIEW

Optical control of molecular switches

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We review recent applications of quantum control on molecular switches by optical means. We discuss diverse examples, as detection and automatic switching between nucleotide base-pairs and their undesired mutants, controlled operation of multi-configurational molecular devices for quantum information storage, and switching between the two enantiomeric forms of a chiral molecule. The variety of examples discussed demonstrates the wide range of applicability and the power of optical quantum control techniques in the fast emerging field of molecular devices.

Keywords: quantum control; molecular switches; laser pulses; multiple equilibrium configurations; genome manipulation; chirality switch

1. Introduction

The fast expanding field of molecular devices investigates compounds with physical and chemical properties of particular interest for the development of analogues of macroscopic devices on the molecular scale. Such properties include the facilitation of electric charge transport, optical response in a controllable fashion, and possible switching between several molecular configurations, just to name a few. The molecular compounds with such properties have numerous potential applications in different areas, as diverse as molecular electronics [1–3], molecular machines and motors [4–12], nano-medical technology [13–15], and quantum information storage [16–18] and processing [19].

The research area of quantum control (QC) is investigating ways to induce the complete transfer of population from an arbitrary initial state to a desired 'target' state by optical means. It consists of various fields, such as coherent control (CC) [20], optimal control [21–26], adiabatic passage (AP) [27,28], and in particular the stimulated Raman adiabatic passage (STIRAP) [29–31], as well as other techniques expanding on elements of these approaches [32].

The integration of the QC methodology into the development of molecular devices is one of the most promising venues in contemporary interdisciplinary science. The possibility of active control on such devices opens new ways, beyond the mere synthesizing of compounds with useful properties. Moreover, due to the extreme advance of laser technology, the QC methods provide perhaps the most powerful means for manipulation on molecular scale, since parameters as frequency, phase, intensity, polarization, and duration of a laser pulse are highly tunable.

In this article, we review recent applications of the QC methodology on control of molecular devices, which are analogues of macroscopic switches, i.e. they exhibit two or more operational modes, directly related to different stable molecular configurations. The examples presented belong to different areas of nano-technology, as well as they involve different techniques for implementing switching on molecular scale by optical means.

This review is organized as follows: in Section 2 we present optical switching between natural and mutant nucleotide base-pairs on the well studied nucleic acid base-pair model – the 2-pyridone and 2-hydroxypiridine hydrogen-bonded dimer [33]. This example could have significant applications in nano-medicine. The switching between the two nucleotidic forms is based on a phase-sensitive three-laser pulse sequence, which is able to 'distinguish' between the natural and mutant configuration of the nucleotide base-pair, although these two compounds possess identical spectroscopic properties. In Section 3, an analytical solution to the problem of determining the proper laser

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parameters for switching the population between several energetically degenerate equilibrium configurations of a molecular compound is presented [34]. The method is exemplified on the Jahn–Teller Al₃O molecule, which has three equivalent minimum configurations. Such systems have potential application as quantum information storage devices. The last example of optical control of molecular switching is discussed in Section 4, where the controlled interconversion between the two forms of a chiral molecule, the *enantiomers*, by simple laser pulses, exemplified on the transiently chiral H_2S_2 molecule, is presented [35]. Switching between the two transient enantiomers of H_2S_2 is induced by a resonant two-photon process. Lastly, we summarize in Section 5.

2. Switching nucleotide base pairs

Hydrogen bonding between nucleotide pairs is a major factor in the observed stability and fidelity of replication of DNA [36]. It has been recognized for quite some time that double proton transfer (DPT) between hydrogen-bonded di-nucleotides can transform one di-nucleotide pair to another, leading to loss of recognition of the correct base pair in DNA and RNA. For example, proton transfer in the Guanine–Cytosine (G·C) pair is considered a crucial part of the radiation-induced damage to DNA [37,38].

The mechanism of the tautomerization of hydrogen-bonded base-pairs, induced by DPT from one stable configuration A to another (almost energetically equivalent) stable configuration B, in either a sequential or concerted fashion, has been discussed in the literature [39–51]. Control over the DPT process is a major objective, as well as techniques that would enable the detection and repair of an undesired tautomerization once it has occurred [13].

We now demonstrate by computational means that phase-coherent laser techniques enable one to both distinguish between base-pairs residing in two energe-tically equivalent A and B minima, as well as induce and control the inter-conversion of the system between these two configurations.

2.1. The di-nucleotide pair model system

As a vehicle for this demonstration we choose the well studied [44–50] nucleic acid base-pair model – the 2-pyridone (2PY) and 2-hydroxypiridine (2HP) dimer (shown in the upper part of Figure 1) embedded in



Figure 1. Top: the di-nucleotide dimer; the double proton (cyan) transfer takes place between the two nitrogen atoms (green) and the two oxygen atoms (red). Bottom: the two-dimensional potential energy surface used in this work. The *s* curvilinear coordinate describes the in-plane double proton transfer motion and the ζ curvilinear coordinate corresponds to the instantaneous out-of-plane normal mode of the two protons along the *s* coordinate. (The color version of this figure is included in the online version of the journal.)

a 'pocket' of a nucleic acid. We keep the dimer at a separation similar to that found in nucleic acids, where the base-pair members are unable to approach each other too closely due to their attachments to the nucleotide backbone [51]. In this way we slow down the natural rate of DPT tunneling in isolated dimers, in keeping with environments typical of base-pairs embedded in nucleic acids.

The concerted motion of the two protons during the 2PY-2HP tautomerization process may be described as a motion along a *linear reaction path* [52] connecting the two equilibrium configurations Aand B. This path is given as,

$$\mathbf{R}_{i}(s) = \frac{1}{2} \left(\mathbf{R}_{i}^{A} + \mathbf{R}_{i}^{B} \right) + s \left(\mathbf{R}_{i}^{B} - \mathbf{R}_{i}^{A} \right), \tag{1}$$

where \mathbf{R}_i^k denotes the three-dimensional Cartesian coordinate vector of the *i*th atom in the molecular center-of-mass frame for the (k = A, B) equilibrium structures. The parameter $-0.825 \le s \le 0.825$ describes the position of the system along the linear reaction path, with the *A* tautomer corresponding to s = -0.5, the *B* tautomer to s = 0.5, and the 'transition state' corresponding to s = 0. This type of path is particularly suitable for studying the transfer of light particles between two heavier moieties [52], which are thus naturally kept practically immobile.

The potential energy and the molecular structures are obtained in an *ab initio* way using the hybrid B3LYP density functional (DFT) method and the valence triple-zeta 6-311++G(d,p) basis set of the *Gaussian* electronic structure calculation package [53]. The two equilibrium configurations of the dimer are planar in the (x, y) plane at this level of *ab initio* theory and consequently the linear reaction path from *A* to *B* is planar as well.

In addition to the in-plane motion we also consider the out-of-plane vibration of the two protons as the system propagates along the reaction path. The instantaneous out-of-plane normal mode along the linear reaction path is chosen in such a way that it overlaps maximally with the $v_{28} \approx 932 \text{ cm}^{-1}$ normal mode of the equilibrium configuration *A* or *B*. This out-of-plane motion is parametrized by a variable $-1 \le \zeta \le 1$. Our working space is thus confined to the $\{(s, \zeta) \in [-0.825, 0.825] \times [-1, 1]\}$ two-dimensional part of the dimer configuration space. This is the minimal space needed to properly describe the dynamics of our control scheme using the energetically lowest states of the dimer.

Our calculations yield a linear reaction path potential-energy barrier height of $\approx 8550 \text{ cm}^{-1}$. Our two-dimensional configuration space model predicts tunneling times from A to B of $\approx 0.15 \, \mu s$. Although this is still much shorter than the estimated tunneling times in nucleic acids [54], it is by far longer than the tunneling times in the isolated unconstrained dimers where the monomers are allowed to get much closer to one another [49,50]. As shown in the following, this tunneling time is sufficiently long to allow us to consider the localized states at the A or B minima as 'legitimate' initial or final states.

Our calculated potential energy and electric dipole surfaces in the $\{s, \zeta\}$ space are shown in Figure 1 (lower panel) and Figure 2. The fact that there exist degenerate A and B tautomers makes the separate addressing of these tautomers by optical means difficult. We have overcome this difficulty using a two step approach: in the first step we affect the discrimination between the tautomers. In the second step we use the discrimination afforded by the first step to control the *interconversion* between the tautomers. The discrimination step [55-58] makes use of the different symmetries of the x, y and z components of the dipole moment to manipulate molecules in configuration A and B differently. As can be seen in Figure 2, the x component of the electric dipole is symmetric with respect to ζ inversion and antisymmetric with respect to s inversion; the z component behaves in the opposite manner; and the *y* component (not shown) is symmetric with respect to inversion of ζ or s.

2.2. Detection and automatic repair

The cyclic laser coupling scheme, which is at the heart of the first 'discrimination' step, is depicted in the upper part of Figure 3. As shown in the figure, the laser fields inter-couple three vibrational states of the *A* tautomer, as well as inter-couple separately three vibrational states of the *B* tautomer. As discussed below, we can, by controlling one overall phase of the laser fields [55–58], excite only the $|1\rangle_B$ ground state to a higher $|i\rangle_B$ vibrational state of the *B* tautomer, while leaving all the *A*-tautomer states untouched.

Following this selective excitation, it is now possible to transfer in the second 'interconversion' step the $|1\rangle_A$ (ground state of the *A* tautomer) population, if such exists, to a $|j\rangle_B \neq |i\rangle_B$ *B*-tautomer excited state. In this way, any population residing initially in $|1\rangle_A$, is automatically converted to the *B* tautomer. Thus, we are able both to detect the existence of a mutation *and* to repair it automatically.

Moreover, if it is the A tautomer that we desire, we can, by tuning the overall laser phase, interchange the process, with the excitation of the B states switched over to the excitation of the A states and the transfer occurring from B to A.



Figure 2. The two-dimensional surface for the x component (upper panel) and z (lower panel) component of the electric dipole 2D configuration space of the di-nucleotide dimer. (The color version of this figure is included in the online version of the journal.)

2.3. The dynamics of detection

We now present a numerical demonstration of the detection scheme. As our localized vibrational states we use the three lowest, $\{|1\rangle_k, |2\rangle_k, |3\rangle_k\}$, k = A, B tautomeric states. The two-dimensional $\{s, \zeta\}$ configuration space wave functions, corresponding to these six localized states, are shown in the middle and bottom panels of Figure 3. Each of the above localized states is a superposition of an $|i'\rangle$ and an $|i''\rangle$ vibrational eigenstate,

$$|i\rangle_{k} = \frac{1}{2^{1/2}} \Big(|i'\rangle \pm |i''\rangle \Big), \quad k = A, B, \tag{2}$$

where $|i'\rangle$ denotes the *s*-symmetric *i*th vibrational eigenstate, and $|i''\rangle$ – the *s*-antisymmetric *i*th eigenstate. Since the dimer in our study is assumed to represent a base-pair confined to a 'pocket' of a nucleic acid, we

are justified in neglecting the rotational motion of the dimer.

According to our calculations,¹ with $q_1 = s$ and $q_2 = \zeta$, the tunneling splittings between the $|i'\rangle$ and $|i''\rangle$ eigenstates for the first three doublets (i = 1, 2, 3) are 10^{-4} , 3×10^{-4} and 10^{-3} cm⁻¹, respectively. These numbers imply that the interconversion times between the $|i\rangle_A$ and $|i\rangle_B$ (i = 1, 2, 3) localized states are roughly 150, 50 and 15 ns, respectively. The laser pulses for our two-step control scheme, 'discriminator' and 'converter' in tandem, are of total duration ≈ 300 ps, which is much shorter than the tunneling interconversion times, thus justifying the assumption that the localized states are well defined physical entities.

The 'discrimination' step depends on the Rabi frequencies associated with each pulse, $\Omega_{ij} = \mu_{i,j} \cdot \mathbf{E}(t) = \Omega_{ii}^{max} f_{i,j}^{l}(t)$, (we use $\hbar = 1$ throughout



Figure 3. The detection scheme. Top panel: the coupling scheme for the discriminator. Middle panels: the $|j\rangle_B$, (j = 1, 2, 3) localized states (left to right). Bottom panels: the $|j\rangle_A$, (j = 1, 2, 3) localized states (left to right). (The color version of this figure is included in the online version of the journal.)

this article, except where otherwise stated), where $\mu_{i,j}$ is the electric dipole moment for the $i \leftarrow j$ transition and E(t) is the electric field of the laser pulse. The time dependence of Ω_{ij} is given by the pulse shape function $f_{ij}^{l}(t)$, shown in the upper panel of Figure 4 for the polarizations used.

The primary factor that allows us to distinguish between the case where the population resides initially in tautomer *A* and the case where it resides initially in tautomer *B* is the phase of the product of the three (complex) Rabi frequencies $\Omega_{23}^k \Omega_{13}^k \Omega_{12}^{k}$ (k = A, B). As shown elsewhere [55–58], by merely changing this phase by π we determine whether it is the *A* or the *B* tautomeric states that are to be affected by the lasers. Here, a π -phase dependence originates in the different symmetry properties of the electric dipole component of the dimer, shown in Figure 2. Due to these different directional properties of the dipole moments, choosing the polarization of the pulse coupling the $|1\rangle_k$ and $|3\rangle_k$ (k = A, B) states to lie along the *x*-direction, and that of the two other pulses to lie along the *z*-direction, results in $\Omega_{1,2}^A = \Omega_{1,2}^B$, $\Omega_{2,3}^A = \Omega_{2,3}^B$ and $\Omega_{1,3}^A = -\Omega_{1,3}^B$. Hence, there exists a π phase difference in the product of the Rabi frequencies as seen by the *A* tautomer relative to that seen by the *B* tautomer. The discrimination process described above is therefore possible.

Our numerical simulation, with electric dipole matrix elements for the relevant $i \leftarrow j$ transitions being ≈ 0.01 Debye, and the chosen pulse intensities yielding $\Omega_{ij}^{\max} \approx 1 \text{ ps}^{-1}$, are plotted in Figure 4. As demonstrated in the upper panel, in order to attain complete population transfer by adiabatic passage, we apply the pulses in a 'counter-intuitive' order [29–31]. By the term 'counter-intuitive' we mean that the $\Omega_{2,3}^z(t)$ 'dump' pulse is applied before the $\Omega_{1,2}^x(t)$ pulse has to last longer than the $\Omega_{1,3}^z(t)$ pulse, and its late part be chirped [55–58] according to $\exp\{-it\Omega_{12}^{\max}\exp[-(t-6\tau)^2/\tau^2]\}.$

As shown in the lower panels of Figure 4 by employing the above pulse ordering we can indeed discriminate between the tautomers: at the end of the



Figure 4. The detection scheme dynamics. Upper panel: the pulse shape functions $f_{ij}^l(t)$ for the laser fields coupling resonantly the localized $|i\rangle_k$ and the $|j\rangle_k k = A, B$ states. The polarization is denoted as l(l=x, z). Middle panels: the initial $(t=-3\tau)$ and final $(t=7\tau)$ wave functions in configuration B. Bottom panels: the same for the A configuration. (The color version of this figure is included in the online version of the journal.)

process the A tautomer is seen to remain in the initially populated (ground) state, while the B tautomer is transferred from its ground state to the $|2_B\rangle$ state. Emptying the ground $|1_B\rangle$ state population, as we have done in the discrimination step, enables us now, in a second step, to exclusively transfer the population from the $|1_A\rangle$ state to the $|3\rangle_B$ state.

2.4. Automatic repair dynamics

The goal of the repair scheme is that the initial population of the $|1_A\rangle$ ground level is transferred to the $|3\rangle_B$ level. The population at the end of the two steps is thus divided between the $|2\rangle_B$ and $|3\rangle_B$ states, thus converting *all* the population from the undesired tautomer *A* to the desired tautomer *B*.



Figure 5. The repair scheme. Upper panels: the eigenfunction of level $|4'\rangle$ (left) and level $|4''\rangle$ (right). Bottom panel: the level scheme considered and the corresponding couplings. (The color version of this figure is included in the online version of the journal.)

This is achieved via a transient excitation to two higher lying eigenstates (shown in Figure 5) that are spaced $\approx 1.1 \text{ cm}^{-1}$ apart, denoted, $|4'\rangle$, which is symmetric, and $|4''\rangle$, which is antisymmetric, with respect to the *s* reaction coordinate. The electric dipole matrix elements connecting the localized states to these eigenstates have been calculated by us to be ≈ 0.005 Debye.

The time dependence of the pulses, hence the Rabi frequencies, is given for the 'converter' step as, $\Omega_{1_k4'} = \Omega_{1_k4'}^{\max} \exp[-(t-11\tau)^2/\tau^2]$, $\Omega_{3_k4'} = \Omega_{3_k4'}^{\max} \exp[-(t-9\tau)^2/\tau^2]$, $|\Omega_{1_k4'}| = |\Omega_{1_k4''}|$ and $|\Omega_{3_k4'}| = |\Omega_{3_k4''}|$, (k = A, B). All the pulses are polarized along the *x* direction, and $\Omega_{i4'}^{\max} \approx 100 \text{ ps}^{-1}$ (i = 1, 3).

In Figure 6 we show the time evolution of the total wave function $|\psi(s,\zeta,t)\rangle = c_{4'}(t)|4'\rangle + c_{4''}(t)|4''\rangle + \sum_{k=A,B}(c_{1_k}(t)|1\rangle_k + c_{3_k}(t)|3\rangle_k)$ during the 'converter' step, integrated over the ζ coordinate

$$\psi(s,t) = \int |\psi(s,\zeta,t)|^2 \,\mathrm{d}\zeta. \tag{3}$$

The population transfer from state $|1_A\rangle$ to state $|3_B\rangle$ is achieved by choosing the pulses in such a way that either $\Omega_{1_k4'}/\Omega_{1_k4''} = -1$ or $\Omega_{3_k4'}/\Omega_{3_k4''} = -1$ (k = A, B) [55–58]. We note that, as in other adiabatic passage schemes [29–31], the $|4'\rangle$ and $|4''\rangle$ states, though being an indispensable part of the 'converter' scheme, are never populated during the entire process [55–58].

We find that after the 'discriminator' and 'converter' steps, all the population in tautomer A has been converted to tautomer B. As mentioned above, by simply changing the phase of one of the Rabi frequencies involved, we could equally well have ended up with only the A tautomer being populated. In fact, our method is capable of purifying a mixture in which there is an initial population in both tautomers. In a complementary way, our approach can be also used on the single-molecule level to identify, for a given dimer, if the ground state configuration is that of A or B.



Figure 6. The time evolution of the wave function $\psi(s, t) = \int |\psi(s, \zeta, t)|^2 d\zeta$ during the 'converter' scheme. (The color version of this figure is included in the online version of the journal.)

3. Switching in multi-configurational molecular compounds

The CC techniques use multiply interfering quantum pathways [20], to selectively transfer population to desired target states. In a complementary way, AP methods [27–31] enable the complete population transfer between quantum states. Recently both techniques have been merged [32], to achieve both selectivity and completeness.

The extension of the three-state STIRAP [29–31] to act on wave packets composed of many non-degenerate states is a crucial first step toward developing universal quantum control techniques. Therefore, the 'non-degenerate quantum control' problem, i.e. how to achieve a complete population transfer between an arbitrary initial $|\Psi_i\rangle = \sum_k c_{i,k} \exp(-i\omega_k t)|k\rangle$ and a target $|\Psi_f\rangle = \sum_{k'} c_{f,k'} \exp(-i\omega_{k'} t)|k'\rangle$ wave packet, formed of non-degenerate quantum states, has been addressed [59] firstly. This transfer is realized by a multi-path two-photon process, proceeding via a single intermediate eigenstate, to which all the non-degenerate states are resonantly coupled by the laser fields.

The way leading to a complete control of quantum systems has been further paved by addressing the 'degenerate quantum control' (DQC) problem [34], i.e. how to transfer population between arbitrary wave packets, $|\Psi_i\rangle \approx \exp(-i\omega_i t)\sum_k c_{i,k}|k\rangle$ and $|\Psi_f\rangle \approx \exp(-i\omega_f t)\sum_k' c_{f,k'}|k'\rangle$, composed of *nearly-degenerate* energy eigenstates, for which the nearest-neighbor separations are much smaller than the bandwidth of the laser pulses used. We can separately address many nearly-degenerate levels, $|k\rangle$ and $|k'\rangle$, by coupling them differently to many non-degenerate eigenstates, $|j\rangle$ and $|j'\rangle$, that form intermediate states of the applied two-photon processes. By being able to control arbitrary wave packets, we significantly extend

previous studies addressing the preparation of selected degenerate superposition states [60–62], as well as open new possibilities for control of multi-configurational molecular compounds to be used as nano-scale devices.

3.1. Analytical solution of the DQC problem

We solve the DQC problem in two-steps, illustrated in Figure 7. In step 1 (left panel), we use a pair of laser pulses to adiabatically transfer the population of the initial wave packet $|\Psi_i\rangle(|1\rangle_{loc})$, composed of the nearlydegenerate energy eigenstates $|k\rangle$ (k = n + 1, ..., 2n), to a single ('parking') state $|0\rangle$, using the non-degenerate auxiliary states $|j\rangle$ $(j=1,\ldots,n)$ as intermediates. The 'dump' (D) pulse, linking the $|j\rangle$ states and the $|0\rangle$ state, characterized by Rabi frequencies $\Omega_{1,\ldots,n;0}$, is followed by a 'pump' (P) pulse, linking the $|k\rangle$ states with all the $|j\rangle$ states, characterized by $\Omega_{n+1,\ldots,2n;1,\ldots,n}$. In step 2 (right panel), the population in the 'parking' state $|0\rangle$ is transferred, by timereversing the dump and pump pulses of step 1 and using different Rabi frequencies, to the target wave packet $|\Psi_f\rangle(|2\rangle'_{loc})$, composed of (the same or a different) set of nearly-degenerate eigenstates $|k'\rangle$.

We now describe the pulses used in DQC. In the first step the total electric field is

$$E(t) = \operatorname{Re} \sum_{j=1}^{n} \left\{ E_{0,j}(t) \exp(-i\omega_{0,j}t) + E_{j,i}(t) \exp(-i\omega_{j,i}t) \right\},$$
(4)

while in the second step $i \rightarrow f$, and the roles of the dump (D) and pump (P) pulses are reversed. The (dump) $E_{0,j}(t) = \hat{\epsilon}_{0,j} E_{0,j}(t)$ and (pump) $E_{j,i}(t) = \hat{\epsilon}_{j,i} E_{j,i}(t)$ field components are characterized by the polarization directions $\hat{\epsilon}_{j,i}$ and the (slowly



Figure 7. The DQC scheme. (Left panel) Step 1: population in a space-localized wave packet $|1\rangle_{loc}$, composed of *n nearly-degenerate* eigenstates is transferred to a single state $|0\rangle$, by a two-photon adiabatic passage via *n non-degenerate* intermediate states. (Right panel) Step 2: population transfer by a time reversed process with different Rabi frequencies from $|0\rangle$ to the target wave packet $|2\rangle'_{loc}$, composed also of a set of nearly-degenerate eigenstates. (The color version of this figure is included in the online version of the journal.)

varying) amplitudes $E_{0,j}(t)$ and $E_{j,i}(t)$. The central frequencies of the field components are chosen to be in near resonance with the system's transition frequencies, $\omega_{0,j} = \omega_0 - \omega_j$ and $\omega_{j,i} = \omega_j - \omega_i$. The complex Rabi frequencies expressed in atomic units are $\Omega_{j,i}(t) \equiv \mathbf{\mu}_{j,i} \cdot \mathbf{E}_{j,i}(t)$, where $\mathbf{\mu}_{j,i}$ are the transition-dipole matrix elements. They have common time envelopes, $\Omega_{j,i}(t) = \mathcal{O}_{j,i}, f_D(P)(t)$, with f_D preceding f_P in both steps.

The system's wave function can be expanded in each step as, $|\Psi\rangle = \sum_{i=0}^{2n} c_i(t)\exp(-i\omega_i t)|i\rangle$, where the column vector $\mathbf{c}(t) = (c_0, c_1, \dots, c_n, c_{n+1}, \dots, c_{2n})^{\mathrm{T}}$, where the superscript T designates the matrix transpose, of coefficients is obtained by solving the matrix Schrödinger equation, $\dot{\mathbf{c}}(t) = -iH(t) \cdot \mathbf{c}(t)$. Here, H(t)denotes the effective Hamiltonian in the rotating wave approximation (RWA) [63],

$$H(t) = \begin{pmatrix} 0 & \boldsymbol{\Omega}_0 & \boldsymbol{0} \\ \boldsymbol{\Omega}_0^{\dagger} & \boldsymbol{0} & \mathbf{H}_F \\ \boldsymbol{0} & \mathbf{H}_F^{\dagger} & \boldsymbol{0} \end{pmatrix}, \quad \mathbf{H}_F = \begin{pmatrix} \boldsymbol{\Omega}_1 \\ \dots \\ \boldsymbol{\Omega}_n \end{pmatrix}, \qquad (5)$$

and

$$\boldsymbol{\Omega}_0 = (\Omega_{0,1}, \dots, \Omega_{0,n}),$$

$$\boldsymbol{\Omega}_j = (\Omega_{j,n+1}, \dots, \Omega_{j,2n}), \quad j = 1, \dots, n,$$
(6)

with [†] denoting the adjoint operation. The Ω_{0-n} vectors of Rabi frequencies are different in the two steps, because they control the population transfer between different wave packets.

The two DQC steps can re/address arbitrary wave packets only if the Rabi vectors $\{\Omega_1, \ldots, \Omega_n\}$, which couple the $(k = n + 1, \ldots, 2n)$ nearly-degenerate levels to the $(j = 1, \ldots, n)$ non-degenerate levels, are linearly independent. In this case, $\mathcal{D} \equiv \det(\mathbf{H}_F) \neq 0$ and the Hamiltonian H(t) has just *one* zero eigenvalue, with the corresponding ('null' or 'dark') eigenvector being given as $(1, 0, \mathbf{x})$, where **0** denotes an *n*-dimensional zero vector and **x** is an *n*-dimensional vector given as $\mathbf{x} = -\mathbf{H}_F^{-1}\mathbf{\Omega}_0^{\dagger}$. Direct operation of $\mathbf{H}(t)$ on $(1, 0, \mathbf{x})$ confirms that this is the null state.

If the Ω_0 vector of Equation (6) is proportional to the *k*th column of the \mathbf{H}_F matrix, i.e. $\Omega_{0,i}^* \propto \Omega_{i,k}$ (i = 1, ..., n), the $(1, 0, \mathbf{x})$ vector correlates at the end of step 1 (start of step 2) with the $|0\rangle$ state and at the start of step 1 (end of step 2) with the $|n+k\rangle$ nearlydegenerate state. The linearity of the above equations guarantees that with the choice $\Omega_{0,i}^* \propto \sum_{k=1}^n a_k^* \Omega_{i,k}$ the null state is correlated at the start of step 1 (end of step 2) with the $\sum_{k=1}^n a_k |n+k\rangle$ superposition state. Thus, complete control over the population transfer between arbitrary wave packets, composed of nearly-degenerate states, can be achieved.

We note that the second step of DQC can be executed effectively only if all the nearly-degenerate final $|k\rangle$ states are initially empty. If these states are populated at the start, $|\Psi_{\rm f}\rangle = \sum_{k=n+1}^{2n} c_k^f |k\rangle$ (all $c_k^f \neq 0$), the vector amplitude $\mathbf{c}^{(f)}$ can not be orthogonal to all the *n* linearly independent vectors $\mathbf{\Omega}_l$, which make up the dump pulse, and they are thus depopulated from the start.

3.2. The Al₃O molecule

We can apply DQC on molecular systems with several quasi-stable (symmetry-related) configurations of equal energies. For example, chiral molecules possess two such configurations [55–58], while more configurations can be found in Jahn–Teller molecules [65]. As a particular example, we consider the Al₃O molecule, which has three local energy minima [66,67]. As shown in Figure 8, they are characterized by $C_{2\nu}$ planar T-shaped geometries, separated by three planar saddle points with $C_{2\nu}$ Y-shaped configurations [66,67]. In order to achieve the desired transfer (pseudo-rotation) between the three T-configurations, we hinder the

overall rotation by (loosely) binding the molecule to a larger system, such as a solid surface or the inside of a large (inert) molecular 'pocket' [68,69]. By doing so, we also orient the Al_3O molecule in such a way that the



Figure 8. The three Jahn–Teller minimum configurations of the Al₃O molecule with XY_3 symmetry are shown, as well as the three intermediate saddle point structures. In the center, we present schematically the potential along the coordinates for the molecular isomerization (*s* direction) and the motion of the X unit out of the Y_3 plane (*z* direction). (The color version of this figure is included in the online version of the journal.)

out-of-plane motion of the O atom relative to the Al_3 triangle coincides with the *z*-direction.

The three quasi-stable T-configurations result in a set of triplet in-plane vibrational states. For energies well below the isomerization barrier, the eigenstates in each triplet are nearly-degenerate and thus can be superimposed into three states that coincide with the three T-configurations, in the considered timescale of the experiment. At the same time, eigenstates in triplets of higher energies are no longer nearly-degenerate. Thus, in principle, the states needed in DQC are readily available, but we still need to pick those that assure the linearly independent coupling. A direct option is to use additional states related with the *out-of-plane* vibrational mode, coupled by the *z*-polarized light, as described below.

We obtain, using *ab initio* methods, the potential surface of a two-dimensional (2D) subspace of the full (6D) configurational space of Al₃O, as shown in Figure 9(*a*). In the same figure, we also present the two-dimensional surface for *x* (*b*), *y* (*c*) and *z* (*d*) components of the electric dipole. The 2D potential energy and electric dipole surfaces are obtained at the PUMP2 level of theory using the 6-31G* basis set [53]. However, the minimum and saddle point molecular structures are optimized at the PUMP2(full) level of theory [53] with the same basis set as before. The 2D subspace includes as one coordinate, denoted by *s*, the



Figure 9. The potential and electric dipole surfaces of our model. Upper panels: the two-dimensional potential energy surface (a) and the surface for the x component of the electric dipole (b). Lower panels: the two-dimensional surfaces for the z (c) and y (d) components of the electric dipole. (The color version of this figure is included in the online version of the journal.)



Figure 10. (a) The three lowest energy eigenstates of the system in the s and z molecular coordinates. (b) Superpositions of these eigenstates form localized states about each Jahn-Teller well. (c), (d) The used intermediate and parking states of DQC, respectively. (e) Time-dependent DQC dynamics of the transfer between the first and second wells. (The color version of this figure is included in the online version of the journal.)

motion along the minimum energy path for isomerization, and as the other coordinate, the out-of-plane bending mode motion of Al₃O along the *z* axis. The height of the isomerization barrier thus obtained, $\approx 320 \text{ cm}^{-1}$, is in good agreement with previous calculations [66,67]. Since the energy of the equilateral D_{3h} -symmetric Al₃O structure is very high, $\sim 9200 \text{ cm}^{-1}$ [66,67], the inclusion of only the ground electronic surface should be sufficient for evaluation of the lower-energy end of the vibrational spectrum. We thus also neglect here geometrical phase effects [70].

The vibrational levels for both the isomerization (s) and the out-of-plane (z) modes appear in triplets, according to our calculations,¹ with $q_1 = s$ and $q_2 = z$.

Each triplet can be characterized by the $\{v_s, v_z\}$ numbers of nodes in each of the three wells and the particular mode. Each triplet contains two degenerate and one separated eigenstates, where the level order alternates from triplet to triplet, with the lowest eigenstate being non-degenerate. In the lowest triplet $\{0, 0\}$, the level separation, $\Delta E \approx 2 \times 10^{-5} \text{ cm}^{-1}$, determines the tunneling time, $\tau_i = 1/\Delta E \approx 1.6 \text{ µs}$, between the three configurations of the molecule. These three eigenstates $|k\rangle$ (i=1,2,3) are shown in Figure 10(*a*). We superimpose them to form the initial and final broken-symmetry wave packets, $|\Psi_i\rangle = \sum_k c_{i,k} |k\rangle$ (i=1,2,3), that are localized in the three Jahn–Teller wells, as displayed in (*b*). The three non-degenerate delocalized states in the $\{4, 0\}$, $\{6, 0\}$ and $\{4, 1\}$ triplets are chosen as the $|j\rangle$ intermediate states, shown in (c). Finally, the non-degenerate state in the $\{6, 1\}$ triplet, presented in (d), is used as the 'parking' state $|0\rangle$.

3.3. The dynamics of the DQC

The light pulses which couple the states must be quite different. Thus, the three non-degenerate intermediate states {4, 0}, {6, 0} and {4, 1} are coupled to the nearly-degenerate localized states $|\Psi_i\rangle$ by pulses polarized in the *x*, *y* and *z* directions, respectively, while they are coupled to the parking $|0\rangle$ state by pulses polarized in the *z*, *z* and *y*(*x*) directions, respectively. In this way we are able, despite the high symmetry of the Al₃O molecule, to tune the field amplitude to achieve the required linear independence of the Ω_1 , Ω_2 , and Ω_3 Rabi vectors, in the DQC steps.

The Rabi frequency amplitudes for both DQC steps are $\Omega_{j,k}(t) = \Omega_{j,k}^{\max} \{ \exp[-(t+\tau)^2/\tau^2] + \exp[-(t-\tau)^2/\tau^2] \}$ and $\Omega_{k,0}(t) = \Omega_{k,0}^{\max} \{ \exp[-(t+3\tau)^2/\tau^2] + \exp[-(t-3\tau)^2/\tau^2] \}$, with $\Omega_{j,k}^{\max} = \Omega_{k,0}^{\max} = 0.2 \text{ cm}^{-1}$ and $\tau = 5 \text{ ns}$. The dipole elements are of the order $10^{-3}-10^{-1}$ Debye. The duration of laser pulses is roughly $8\tau \ll \tau_i$, so that the $|\Psi_i\rangle$ states remain localized in their corresponding potential wells for sufficiently long time to be used as the initial states of the DQC scheme.

We display the time evolution of the system, during the two steps of the DQC transfer, in Figure 10(e). The z-integrated probability density $[dz|\langle s,z|\Psi(t)\rangle|^2$ is presented as a function of s and t. We start with the $|\Psi_1\rangle$ localized-state being populated. At the end of step 1, its population is 'parked' to the excited delocalized $|0\rangle$ state, using as intermediate the $|i\rangle = |1\rangle - |3\rangle$ states, that remain unpopulated throughout the process. During a reasonably short parking, the bulk of the probability density is concentrated near the three saddle points, with almost no probability density residing in the three wells regions. Then, at the end of the second step, the parked population is transferred to the localized $|\Psi_2\rangle$ state. We assume that the relaxation time related with the parking state is long enough, so that little population would be lost in a real experiment.

The presented control of the Jahn–Teller isomerization in the Al_3O molecule clearly demonstrates the power of the DQC solution. We can control stable isomers in the same way, if the intermediate states belong to an excited electronic surface. In problems with more nearly-degenerate states to be controlled, we might include other physical degrees of freedom, to assure their linearly independent coupling. Besides its fundamental importance in understanding the degenerate quantum control, the presented approach could be applied in numerous practical systems.

4. Switching of molecular chirality

Molecular chirality is of fundamental importance in nature [71,72]. Therefore, methods for controlling molecular handedness have drawn much attention in chemistry and biology. Since the advances in laser technology numerable studies on control of molecular chirality by optical means have appeared. Earlier suggestions of such methods centered on the use of circularly polarized light [73,74] utilizing the very weak magnetic–dipole interaction between a chiral molecule and an electromagnetic field. However, in recent works, the methods are focused on the far stronger electric dipole interaction [56,57,75–82].

Here, we discuss a simple method for complete enantiomeric conversion of chiral molecules using an analytically solvable model of a Λ -type three-level system at exact two-photon resonance [35,83]. The model is also applicable when the intermediate state is off single-resonant. As in the previous examples discussed, the spontaneous emission is neglected in this model, because the lifetimes of the involved levels are supposed to be much longer than the interaction time with the light pulse. The general scenario is demonstrated on the (transiently) chiral H₂S₂ molecule, which is shown in the upper part of Figure 11.

We also note that the most challenging case of enantiomeric purification of racemic mixtures, i.e. mixtures of left-handed (L) and right-handed (D) enantiomers of a chiral molecule, can be achieved with more advanced methods [56,57], implementing the 'discriminator' and 'converter' steps, discussed in Section 2, or alternatively, using the 'laser distillation' method [75–77].

4.1. The H_2S_2 molecule

The H_2S_2 molecule is depicted in Figure 11 (upper panel), with the *z* axis of the molecule-fixed frame oriented parallel to the principal axis corresponding to the smallest moment of inertia, and the *y* axis of the molecule-fixed frame oriented along the S–S bond of the molecule.

 H_2S_2 has six vibrational degrees of freedom, from which the large amplitude torsional motion about the S–S bond is relevant to stereomutation. In particular, there are two torsional barriers, a *cis* and a *trans* barrier, roughly 2700 cm⁻¹ and 1900 cm⁻¹ in height, respectively [57,84,85]. A one-dimensional cut of the ground electronic potential energy surface along the stereomutation path over the *trans* barrier is shown in



Figure 11. Upper panel: the orientation of the H_2S_2 molecule in the molecule-fixed frame. Lower panel: the double well potential energy along the torsional motion of the H atoms about the S–S bond, used to describe the stereomutation path of the H_2S_2 . (The color version of this figure is included in the online version of the journal.)

the lower part of Figure 11. The experimental tunneling splitting [84] of the lowest torsional level is very small, $\sim 2 \times 10^{-6}$ cm⁻¹, corresponding to an enantiomeric lifetime of $\sim 16 \,\mu$ s. Thus, although H₂S₂ is not a chiral molecule in the conventional sense, a molecular configuration described by superposition of the lowest torsional states, localized in one minimum of the double well potential, stay chiral sufficiently long in order to be detectable. H₂S₂ has C₂ symmetry at its equilibrium structure, but due to tunneling through the two barriers, the symmetry group G_4^{\dagger} is used for energy level classification [86–89]. H₂S₂ is an almost prolate symmetric top [85].

Since stereomutation of H_2S_2 occurs through the internal rotation, the relevant configuration subspace is defined by the minimum energy path of the torsion about the S–S bond, described by the dihedral angle θ between the two SSH planes (upper panel of Figure 11). The *cis* and *trans* conformers of H_2S_2 correspond to $\theta = 0$ and $\theta = 180$, respectively.

The torsional eigenstates are obtained using the minimum energy path of [57], which is obtained by *ab initio* methods at the coupled-cluster level of theory including single and double excitations and a perturbational correction due to connected triple excitations, CCSD(T) [53]. The basis set employed is the correlated-consistent polarized cc-pVTZ [53].

4.2. Dynamics of the degenerate Λ system

We denote $|L\rangle$, $|D\rangle$ the lower degenerate states and $|e\rangle$ the upper state of the Λ -type three-level system interacting with a (nearly) resonant laser field. The corresponding Hamiltonian within the RWA [63], reads

$$H = \Delta |e\rangle \langle e| + \frac{1}{2} [\Omega(t)|L\rangle \langle e| + \Omega(t)|D\rangle \langle e| + \text{H.c.}].$$
(7)

Here, $\Omega(t) \equiv \mathbf{\mu} \cdot \mathbf{E}(t)$ is the Rabi frequency, with $\mathbf{\mu}$ being the matrix element vector for the $|L\rangle (|D\rangle) \leftrightarrow |e\rangle$ transition and $\mathbf{E}(t) = \operatorname{Re}\{f(t)\mathbf{E}_0 \exp(-i\Delta t)\}$ denoting the electric field, with amplitude \mathbf{E}_0 and pulse shape function f(t). Furthermore, $\Delta \equiv \omega_e - \omega_L - \omega = \omega_e - \omega_D - \omega$ stands for the detuning from resonance for the transition $|L\rangle(|D\rangle) \leftrightarrow |e\rangle$, where ω_j is the energy of the $|j\rangle$ level and ω is the angular frequency of the laser field.

We now define two new basis states

$$|C\rangle \equiv \frac{1}{2^{1/2}}(|L\rangle + |D\rangle), \quad |NC\rangle \equiv \frac{1}{2^{1/2}}(-|L\rangle + |D\rangle).$$
(8)

The state $|NC\rangle$ is decoupled from the driving pulse, since $H|NC\rangle = 0$. The Hamiltonian of Equation (7) is now transformed into

$$H = \Delta |e\rangle \langle e| + \frac{1}{2^{1/2}} \bar{\Omega}(t) (|C\rangle \langle e| + |e\rangle \langle C|), \qquad (9)$$

where $\Omega(t) = \Omega(t)/2$. The Hamiltonian of Equation (9) describes the interaction of the two-level system composed of the $|C\rangle$ and $|e\rangle$ levels with a pulsed laser field [63].

The time evolution under the Hamiltonian of Equation (9) can be obtained by the transition matrix method [63,64]. The general transition matrix can be parameterized in the basis $\{|NC\rangle, |C\rangle, |e\rangle\}$ as

$$U(t_{\rm f}, t_i) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \alpha & -\beta^* \\ 0 & \beta & \alpha^* \end{bmatrix},$$
(10)

with $|\alpha|^2 + |\beta|^2 = 1$ [63,64].

Here, we are interested when the system is in state $|L\rangle$ or $|D\rangle$ at t_i , and at the end of the pulse, at t_f , the state $|e\rangle$ is not populated. Hence, the parameters of the transfer matrix $U(t_f, t_i)$ must fulfill

$$\alpha = \exp(-i\delta) \neq 0, \quad \beta = 0. \tag{11}$$

We thus obtain

$$|\psi_{\rm f}\rangle = \langle NC|\psi_{\rm i}\rangle|NC\rangle + \exp(-{\rm i}\delta)\langle C|\psi_{\rm i}\rangle|C\rangle, \qquad (12)$$

as the final state of the process, where δ denotes the acquired phase due to the pulse. Assuming that the system is initially in state $|L\rangle$, we have

$$|\psi_{\rm f}\rangle = \exp\left(-\mathrm{i}\frac{\delta}{2}\right) \left[\cos\frac{\delta}{2}|L\rangle - \mathrm{i}\sin\frac{\delta}{2}|D\rangle\right]. \tag{13}$$

It then follows for the final populations of levels $|L\rangle$ and $|D\rangle$

$$P_L(t_{\rm f}) = \cos^2\left(\frac{\delta}{2}\right), \quad P_D(t_{\rm f}) = \sin^2\left(\frac{\delta}{2}\right).$$
 (14)

Therefore, if the system is initially in the state $|L\rangle$, complete enantiomeric conversion occurs when $\delta = (1 + 2k)\pi$ (k being an integer or zero), corresponding to $\alpha = -1$ in Equation (11).

Under pulsed excitation, the parameters of the transition matrix read

$$\alpha = \cos\left[\frac{1}{2^{1/2}} \int_{t_i}^{t_f} \bar{\Omega}(t) dt\right], \quad \beta = -i \sin\left[\frac{1}{2^{1/2}} \int_{t_i}^{t_f} \bar{\Omega}(t) dt\right].$$
(15)

The simplest case is the rectangular pulse, for which $\overline{\Omega}(t) = \Omega'$ if $0 \le t \le T$, and zero otherwise. The elements of the transition matrix of Equation (10) are given as

$$\alpha = A \exp(-i\Delta T/2), \quad \beta = -iB \exp(-i\Delta T/2), \quad (16)$$

with $A \equiv \cos(\widetilde{\Omega}T/2) + i(\Delta/\widetilde{\Omega})\sin(\widetilde{\Omega}T/2)$, $B \equiv (2^{1/2}\Omega'/\widetilde{\Omega})\sin(\widetilde{\Omega}T/2)$, and $\widetilde{\Omega} \equiv (2\Omega^2 + \Delta^2)^{1/2}$. It follows, that for effective pulse area

$$\tilde{\Omega}T = 2\pi m$$
, with $m = 1, 2, ...,$ (17)

the transition amplitudes become

$$\alpha = \exp\left[-i\left(\frac{\Delta}{\widetilde{\Omega}} + 1\right)m\pi\right], \quad \beta = 0, \qquad (18)$$

thus, fulfilling the conditions of Equation (11). In this case, the angle δ reads

$$\delta = \left(\frac{\Delta}{\widetilde{\Omega}} + 1\right) m\pi. \tag{19}$$

4.3. Degenerate Λ model of H_2S_2 and complete enantiomeric conversion

We now apply the method discussed in Section 4.2 on H_2S_2 . We consider chiral rovibrational ground states

$$|L\rangle = \frac{1}{2^{1/2}} (|0_1\rangle + |0_4\rangle) \mathbf{D}_{0,0}^{0,+}, \quad |D\rangle = \frac{1}{2^{1/2}} (|0_1\rangle - |0_4\rangle) \mathbf{D}_{0,0}^{0,+}.$$
(20)

Here, $D_{\lambda,M}^{J,p}$ are the rotational matrices [90], where *J* is the total angular momentum, *M* is its projection on the laboratory *Z* axis (we use capital letters to denote the laboratory-fixed axes) and λ is its projection on the molecule-fixed *z* axis, $p = \pm 1$, $t_{\lambda} = 2^{-1/2}$ for $\lambda > 0$ and $t_{\lambda} = 1/2$ for $\lambda = 0$. Since H₂S₂ is essentially a prolate symmetric top, the $\mathbf{D}_{\lambda,M}^{J,p}$ functions approximate well the rotational eigenfunctions of H₂S₂ (at least for the low *J* values considered here [35,65]). The torsional eigenstates are characterized in a normal-mode-like manner as $|v_{\tau}\rangle$, which denotes a vibrational quantum number *v*, and a symmetry quantum number $\tau = 1, \ldots, 4$ for each *v* [35].



Figure 12. Left panel: time evolution of the populations in states $|L\rangle$ (solid curve), $|D\rangle$ (dashed curve) and $|e\rangle$ (dot-dashed curve). The evolution is for rectangular pulse with $\Omega' = 0.0125 \text{ cm}^{-1}$, $\delta = 3$, m = 2 and the rest of the parameters are chosen to fulfill Equations (17) and (19). Right panel: pulse duration for complete enantiomeric conversion as function of the intensity *I* for a resonant rectangular pulse. (The color version of this figure is included in the online version of the journal.)

The $|L\rangle \leftrightarrow |D\rangle$ interconversion time accompanying the corresponding tunneling splitting occurs within 16 µs, according to our calculations [35]. Thus, pulses of nanosecond duration are short enough for the $|L\rangle$ and $|D\rangle$ states to be considered chiral. We use the state $|4_4\rangle \mathbf{D}_{0,0}^{1,+}$ as intermediate state $|e\rangle$. The closest states to $|e\rangle$, for which electric dipole transitions from $|L\rangle$ and $|D\rangle$ are allowed, are energetically higher by $\delta E \approx 4.72 \text{ cm}^{-1}$. In the discussion below we always consider field detuning Δ and pulse width values that are much smaller than δE , so that the state $|e\rangle$ can be considered isolated.

Transitions between states of H_2S_2 with $\Delta\lambda = 0$ are induced by the z component of the electric dipole moment, which is antisymmetric with respect to the torsional angle θ [35]. The x and y component of the electric dipole moment vanish along the stereomutation path. We obtain the transition dipole moments $\langle L|\mu_z|e\rangle = \langle D|\mu_z|e\rangle \approx 3 \times 10^{-4}$ Debye using the onedimensional cut along the minimum energy path of the electric dipole surface of [57], which is obtained by ab *initio* methods at the coupled-cluster level of theory including only double excitations, CCD [53], with the *cc-pVTZ* [53] basis set. We note that the $|L\rangle(|D\rangle) \leftrightarrow |e\rangle$ transitions are induced only by irradiation along the Zaxis in the laboratory frame [65] with $\langle k | \mu_Z | e \rangle \approx$ 0.5 $\langle k | \mu_z | e \rangle$, for k = L, D, since $\langle k | \mu_x | e \rangle = \langle k | \mu_y | e \rangle = 0$. Thus, no pre-orientation of the molecules is necessary for our scheme to work.

We first consider the case of resonant pulsed fields. For a rectangular pulse with $\overline{\Omega}(t) = \Omega'$, $0 \le t \le T$, we obtain that complete $|L\rangle \rightarrow |D\rangle$ conversion is achieved for duration $T = \pi m 2^{1/2} / \Omega'$, m = 1, 2, ... according to Equation (17). A typical time evolution of the populations in the three states of the system for complete enantiomeric conversion is shown in the left panel of Figure 12. In the right panel of Figure 12, we show T as a function of the pulse intensity I for m = 1, ..., 5. In the case of a resonant Gaussian pulse $\overline{\Omega}(t) = \Omega_0 \exp(-t^2/\tau^2)$, using $\int_{-\infty}^{\infty} \overline{\Omega}(t) dt = \Omega_0 \tau \pi^{1/2}$ and Equation (15), we obtain that complete enantiomeric conversion $|L\rangle \rightarrow |D\rangle$ is achieved for $\tau = (2\pi)^{1/2} m/\Omega_0$, m = 1, 2, ...

We now focus on the case of a non-resonant rectangular pulse. With Equation (17) and $\widetilde{\Omega} = (2\Omega^{\prime^2} + \Delta^2)^{1/2}$, we obtain that complete conversion $|L\rangle \rightarrow |D\rangle$ is achieved for pulse duration

$$T = m \frac{2\pi}{\Omega'} \frac{x}{(2x^2 + 1)^{1/2}}$$
(21)

with $x = \Omega' / \Delta$. In the left panel of Figure 13 the duration T of the pulse as a function of the detuning Δ for complete conversion $|L\rangle \rightarrow |D\rangle$ is given according to Equation (21) for m=1 and Ω' values of 0.005, 0.0075, 0.01 and 0.0125 cm⁻¹, corresponding to pulse intensity I of 2.5, 5.625, 10 and $15.625 \,\mathrm{GW}\,\mathrm{cm}^{-2}$, respectively. The duration T for $m = 2, 3, \ldots$ values is easily obtained from Figure 13 due to the linear scale relation between T and m as implied by Equation (21). We note that complete enantiomeric conversion at non-zero detuning Δ with this method is possible, as shown in the left panel of Figure 13. In the right panel of the same figure, the efficiency of the enantiomeric conversion, given by $|\alpha|^2$ from Equation (16), is shown for the rectangular pulse, as a function of the pulse area $\Omega'T$ and the scaled detuning ΔT . When $(\Delta/\tilde{\Omega}+1)m =$ odd integer, complete enantiomeric conversion is achieved.

5. Summary

We have presented recent applications of optical control techniques on molecular switching. We have discussed examples related to quantum information storage, biochemistry, and nano-medicine.



Figure 13. Left panel: pulse duration T for complete enantiomeric conversion as a function of the detuning Δ of a non-resonant rectangular pulse for various coupling strength. Right panel: the efficiency of the enantiomeric conversion, given by $|\alpha|^2$ from Equation (16), as a function of pulse area $\Omega' T$ and scaled detuning ΔT . (The color version of this figure is included in the online version of the journal.)

In particular, we have introduced optical methods for controlled population transfer between energetically degenerate states of multi-configurational molecular compounds, as well as controlled interconversion of molecular chirality and the detection and automatic repair of nucleotide base-pair mutations. The variety of the applications discussed demonstrates the power and wide applicability of optical control techniques, and the central role such methods can play in the design and development of molecular devices.

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Note

1. The vibrational eigenstates in a two-dimensional configuration space are obtained in the Discrete Variable Representation (DVR) [91–94] by solving the corresponding Schrödinger equation with a Hamiltonian for the generalized coordinates [65] q_1 and q_2 (with $\partial q_i \equiv i\hbar\partial/\partial q_i$)

$$H = \frac{1}{2} \sum_{q_1, q_2} \partial_{q_1}^* G_{q_1 q_2}(q_1, q_2) \partial_{q_2} + u(q_1, q_2) + V(q_1, q_2).$$
(22)

Here, V is the potential energy of the electronic state considered and u is the 'pseudopotential' [65]

$$u(q_1, q_2) = \frac{1}{8} \sum_{q_1, q_2} \frac{\partial}{\partial q_1} \left\{ G_{q_1 q_2} \frac{\partial \ln |\mathbf{g}|}{\partial q_2} \right\} + \frac{1}{4} \frac{\partial \ln |\mathbf{g}|}{\partial q_1} G_{q_1 q_2} \frac{\partial \ln |\mathbf{g}|}{\partial q_2},$$

where \mathbf{g} is the covariant and \mathbf{G} is the contravariant metric tensor, respectively, given by

$$g_{q_1q_2} = m_a \frac{\partial \mathbf{x}_a}{\partial q_1} \cdot \frac{\partial \mathbf{x}_a}{\partial q_2}, \quad G_{q_1q_2} = m_a^{-1} \frac{\partial q_1}{\partial \mathbf{x}_a} \cdot \frac{\partial q_2}{\partial \mathbf{x}_a}, \tag{23}$$

and $|\mathbf{g}|$ is the determinant of \mathbf{g} . In the above equations, where summation over dummy indices is implicitly understood, m_a is the mass of the *a*th atom in the molecular system, \mathbf{e}_{α} ($\alpha = x, y, z$) are the unit vectors in the center-of-mass molecule-fixed frame and x_a denotes the Cartesian coordinate vector of the *a*th atom in this frame.

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