Distinguishing left- and right-handed molecules using two-step coherent pulses

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Abstract
Chiral molecules with broken parity symmetries can be modelled as quantum systems with cyclic-transition structures. By using these novel properties, we design two-step laser pulses to distinguish left- and right-handed molecules from the enantiomers. After the applied pulse drivings, one kind of chiral molecule is trapped in a coherent population trapping state, while the other is pumped to the highest states for ionization. Then the different chiral molecules can be separated.

(After the addition of the abstract, the text continues with the rest of the paper.)

A chiral molecule lacks an internal plane of symmetry and consequently is not superposable on its mirror image. The coexistence of left- and right-handed chiral molecules (called ‘enantiomers’) originates from the fundamental broken symmetries in nature [1]. The physiological effect of enantiomers of biologically active compounds may vary significantly [2]. In general, only one enantiomeric form has the potential to be biologically beneficial, while the other one could be harmful or fatal. Thus, chiral purification and discrimination of enantiomers are fundamentally important tasks in pharmacology, biochemistry, etc [3].

Traditionally, various chromatographic separation methods, e.g., gas chromatography (GC), high performance liquid chromatography (HPLC), gas liquid chromatography (GLC) and thin layer chromatography (TLC), [4], are widely utilized to achieve enantioseparation. Recently, certain optical means [5–8] were also proposed to implement the desirable purification. In particular, these chiral molecules are quantum systems with broken-parity symmetries and the usual electric-dipole selection rules do not hold. As a consequence, if only the three lowest levels are considered, a chiral molecule (left-handed or right-handed) can be treated as a quantum system with a \(\Delta\)-type cyclic-transition structure. Note that cyclic transitions can also be realized in some other quantum systems, e.g., superconducting artificial atoms [9, 10]. Recent studies have shown that, based on this novel property, by coupling these cyclic-transition molecules with optical fields, new methods such as cyclic population transfer [11, 12], the generalized Stern–Gerlach effect [13] and dynamical control [14], can be used to achieve enantioseparation.

In this paper, we develop a dynamical method by using only two-step ultrashort coherent pulses to implement the desirable enantioseparation. Due to the fact that only dynamical ultrashort-pulse operations are used, the dynamical method will work faster and make decoherence effects less important [14]. In our protocol, both cyclic transition and coherent population trapping (CPT) [15–17] are utilized to achieve enantioseparation. A specific example of the chiral molecules with cyclic transition is the \(D_2S_2\) enantiomers, as shown in [12]. Our basic idea is as follows. First, each enantiomer is prepared at the superposition of the two relatively lower states by applying an ultrashort \(\pi/2\) pulse. Subsequently, two pulses are simultaneously applied to couple these lower states to the highest one. Suppose that the Rabi frequencies of the pulses are chosen appropriately, so that for one kind of chiral molecule, the state prepared in the first-step pulse operation can be just a CPT state during the second-step pulses, while the other kind of chiral molecule is pumped to the highest quantum state after a \(\pi\) rotation. Then, two kinds of chiral molecules can be separated by using ionization, followed by ion extraction by an electric field, as suggested in [11, 14].

The transition structures of chiral molecules considered in this paper are schematized in figure 1. Here, only the three lowest levels in the chiral molecules are considered, and thus each chiral molecule can be modelled as a three-level cyclic...
quantum system [11–14]. Three laser beams are applied to drive the enantiomeric molecules. The Hamiltonian of the system can be written as

\[ H = \sum_{i=1}^{3} E_i |i\rangle \langle i| + \sum_{j,i=1}^{3} \Omega_{ij} e^{-i\omega_{ij}t} |j\rangle \langle i| + \text{h.c.}, \]

where \( E_i \) are the eigenvalues of the energy eigenstates \( |i\rangle \), \( \omega_{ij} \) are the frequencies and \( \Omega_{ij} \) are the Rabi frequencies of the applied coherent driving fields. Note that \( \Omega_{ij} \) should be regarded as complex parameters for the optical responses of quantum systems with loop transition structures which are phase sensitive [11–14, 18]. Let \( \Delta_1 = E_3 - E_1 - \omega_{13} \), \( \Delta_2 = E_2 - E_1 - \omega_{23} \) and \( \Delta_3 = E_3 - E_2 - \omega_{32} \) be the detunings of the applied driving fields. When the resonant condition \( \Delta_i = 0 \) is satisfied, in the interaction picture, the interaction Hamiltonian can be written as

\[ H_I = \sum_{j=1}^{3} \Omega_{ij} |j\rangle \langle i| + \text{h.c.}. \]

One of the typical features in the present cyclic-transition systems is that depending on the polarizations of the fields, one or all of the three Rabi frequencies \( \Omega_{ij} \) for the two kinds of chiral molecules differ by a sign [11, 12], i.e. the total phases of the three Rabi frequencies differ by \( \pi \) between the enantiomers. This means that the left- and right-handed molecules could be distinguished by a phase-dependent dynamical process applied to the enantiomers. Following [12, 14], the Rabi frequencies for driving the left- and right-handed molecules are chosen as \( \Omega_{ij}^L(t) = \Omega_{ij}(t) \), \( \Omega_{ij}^R(t) = -\Omega_{ij}(t) \), \( \Omega_{12}^R(t) = \Omega_{12}(t) \) and \( \Omega_{23}^R(t) = \Omega_{23}(t) \). We assume the initial states of the left- and right-handed molecules are their ground states \( |1\rangle_L \) and \( |1\rangle_R \), respectively. To achieve the desirable enanthsoposphation, the left- and right-handed molecules should be engineered at the quantum states with different energies. To do this, we design the following two-step pulse process shown in figure 2.

Firstly, a \( \pi/2 \) pulse with the Rabi frequency \( \Omega_{12}^L(t) = \Omega_{12}^R(t) = \Omega_{12}(t) \) is applied to the mixture of chiral molecules for producing the superpositions of the lowest two energy states. In this step, \( \Omega_{12}(t) \) is set as a real parameter, i.e. its phase is zero. During this pulse the interaction Hamiltonians for the left- and right-handed molecules read

\[ H_{1}^L = \Omega_{12}|2\rangle_L \langle 1| + \text{h.c.} \]

and

\[ H_{1}^R = \Omega_{12}|2\rangle_R \langle 1| + \text{h.c.}, \]

respectively. Clearly, the chiral molecules undergo the dynamical evolutions

\[ |\Psi_1(t)\rangle_{L,R} = \cos \left( \int_0^t \Omega_{12}(t) \, dt \right) |1\rangle_{L,R} - i \sin \left( \int_0^t \Omega_{12}(t) \, dt \right) |2\rangle_{L,R}. \]

Obviously, if the duration of the applied pulse is designed as \( \int_0^t \Omega_{12}(t) \, dt = \pi/4 \), namely a \( \pi/2 \) pulse, the states of the enantiomers are prepared as \( |\psi_{1L}\rangle = (|1\rangle_L - |2\rangle_L)/\sqrt{2} \) and \( |\psi_{1R}\rangle = (|1\rangle_R - |2\rangle_R)/\sqrt{2} \), respectively.

Secondly, we apply simultaneously two pump pulses coupling transitions \( |1\rangle_{L,R} \leftrightarrow |3\rangle_{L,R} \) and \( |2\rangle_{L,R} \leftrightarrow |3\rangle_{L,R} \) with properly designed Rabi frequencies for evolving the different chiral molecules into different quantum states.

The Rabi frequencies of the second-step pulses could be designed as

\[ \Omega_{13}^L(t) = -\Omega_{13}^R(t) = \Omega_{13}(t) = i\Omega_0(t), \]

\[ \Omega_{23}^L(t) = \Omega_{23}^R(t) = \Omega_{23}(t) = \Omega_0(t), \]

with \( \Omega_0(t) = |\Omega_{23}(t)| = |\Omega_{13}(t)| \). Then accordingly Hamiltonians can be written as

\[ H_{2}^L = \Omega_{L}|3\rangle_L \langle \Phi| + \text{h.c.} \]

\[ H_{2}^R = \Omega_{R}|3\rangle_R \langle \Phi| + \text{h.c.}, \]

with \( |\Phi\rangle_L = (|1\rangle_L + |2\rangle_L)/\sqrt{2}, |\Phi\rangle_R = (|1\rangle_R + |2\rangle_R)/\sqrt{2} \) and the effective Rabi frequency \( \Omega = \sqrt{2}\Omega_0 \). It is easily checked that the state \( |\psi_{1L}\rangle \) is a CPT state for the Hamiltonian (5) with the zero eigenvalue. (Note that \( |\psi_{1L}\rangle \) does not belong to the subspace spanned by \( |\Phi\rangle_L \) and \( |3\rangle_L \). This means that the state \( |\psi_{1L}\rangle \) remains unchanged after this operation, i.e. \( |\psi_{2L}\rangle = |\psi_{1L}\rangle \). For the right-handed molecules prepared in the
the right-handed molecules are totally pumped to the two-step pulses are accurate. At the end of the process, the left-handed molecules are completely trapped in the |3⟩_R state. (c) and (d) The pulse duration in the second step is inaccurate. After pulse operation, the left-handed molecules are not influenced and completely trapped in the |3⟩_R state. (e) and (f) All the pulses, including their durations and the relative phase of the two pulses used in the second step, are inaccurate. (Here we assume that all these quantities exhibit a 10% deviation from ideal values.) After pulse operation, the left-handed molecules are still mostly populated in the |1⟩_L and |2⟩_L states, and the right-handed molecules are nearly pumped to the |3⟩_R state. This shows that the two-step pulse approach is robust, even if the operations are imperfect.

Given the two kinds of chiral molecules evolving to different states with different energies after the above two-step pulses, an ionization process, as suggested in [11], can be utilized to separate them. Specifically, in our case, by appropriate ionization energies, the right-handed molecules prepared in the highest levels can be ionized, but the left-handed ones populating in the superposition of two lower states remain unchanged. Followed by the ion extractions via an electric field, the mixture of enantiomers can be finally separated.

Practically, in the two-step pulse process, the Rabi frequencies, either of the intensities or the phases, may be inaccurate. Now we begin to discuss the influence of all these deviations on enantiopreservation. At first, we assume that in the first step, the applied pulse deviate from the perfect π/2 pulse and accordingly the Rabi frequencies could then be written as \( \tilde{\Omega}_{12} = \tilde{\Omega}_{12}^R = \tilde{\Omega}_{12} = \tilde{\Omega}_{12} + \delta \tilde{\Omega}_{12} \), with \( \int_0^{\tilde{\tau}} \Omega_{12} \, dt = \frac{\pi}{2}, \int_0^{\tilde{\tau}} \delta \Omega_{12} \, dt = \Delta \). Clearly, after this pulse operation, the states of the enantiomers are prepared as

\[
|\psi_1\rangle_{1\ L\ R} = \cos \Delta \frac{1}{\sqrt{2}} (|1\rangle_{1\ L\ R} - i|2\rangle_{1\ L\ R})
- \sin \Delta \frac{1}{\sqrt{2}} (|1\rangle_{1\ L\ R} + i|2\rangle_{1\ L\ R}).
\]  

(8)

In addition, we assume that in the second step, the simultaneously applied two pump pulses are also imperfect ones with the Rabi frequencies \( \Omega_{13}^L(t) = -\Omega_{13}^R(t) = \Omega_{13} = e^{i\phi} (\Omega_0 + \delta \Omega_0) \), \( \Omega_{23}^L(t) = \Omega_{23}^R(t) = \Omega_{23} = \Omega_0 + \delta \Omega_0 \), where \( \delta \Omega_0 \) and \( \delta \phi \) represent the deviations of amplitude and phase of the Rabi frequency, respectively. Let \( \Omega = \tilde{\Omega} + \delta \tilde{\Omega} = \sqrt{2} (\Omega_0 + \delta \Omega_0) \); the effective Hamiltonian describing this step can be written as

\[
|\psi_2\rangle_{2\ L\ R} = -\frac{i}{2} C(t) \left( |1\rangle_{2\ L\ R} - i|2\rangle_{2\ L\ R} \right)
+ \sin \frac{1}{2} C(t) \left( |1\rangle_{2\ L\ R} + i|2\rangle_{2\ L\ R} \right).
\]  

(9)
with $|\Phi'_L\rangle = \frac{1}{\sqrt{2}}(-ie^{i\phi}|1\rangle + |2\rangle)$ and $|\Phi'_R\rangle = \frac{1}{\sqrt{2}}(ie^{i\phi}|1\rangle + |2\rangle)$. We can define the states $|\psi'_L\rangle = \frac{1}{\sqrt{2}}((1 - e^{i\phi})|2\rangle)$ and $|\psi'_R\rangle = \frac{1}{\sqrt{2}}((1 + e^{i\phi})|2\rangle)$, which are orthogonal to $|\Phi'_L\rangle$ and $|\Phi'_R\rangle$, respectively. Thus, the initial states of the left- and right-handed molecules of the second pulse operation can be rewritten as

$$|\psi'_L(2)\rangle_{LR} = A_{1L,R} |\Phi'_L\rangle_{LR} + B_{1L,R} |\psi'_L\rangle_{LR}$$

with $A_{1L,R} = \frac{1}{2}[(\cos\Delta(e^{i\phi} + 1) \pm \sin\Delta(e^{i\phi} + 1)]$ and $B_{1L,R} = \frac{1}{2}[\cos\Delta(1 \pm e^{i\phi}) - \sin\Delta(1 \mp e^{i\phi})]$. Obviously, in the second pulses process, the dynamical evolution of the chiral molecules reads

$$|\psi'_L(2)\rangle_{LR} = A_{1L,R} \cos \left(\int_0^t \Omega' dt\right) |\Phi'_L\rangle_{LR}$$

$$- iA_{1L,R} \sin \left(\int_0^t \Omega' dt\right) |\Phi'_L\rangle_{LR}$$

Clearly, after an imperfect $\pi$ rotation with the effective Rabi frequency $\Omega' = \Omega + \delta \Omega$ (here we assume that $\int_0^t \Omega' dt = \frac{\pi}{2}$), the left- and right-handed molecules evolve to the states

$$|\psi'_L(2)\rangle_{LR} = -A_{1L,R} \sin \Delta' |\psi'_L\rangle_{LR}$$

As a consequence, the final populations of the enantiomers for the small $\Delta, \Delta', \delta\phi$ read

$$p_{1L,2}' = \frac{1}{2} \left[1 - \Delta^2 \pm 2\Delta \Delta' - \frac{1}{4} (\delta\phi)^2\right],$$

$$p_3' \approx \frac{1}{4} (\delta\phi)^2 + \Delta^2,$$

$$p_{1L,2}' \approx \frac{1}{2} \left[\Delta^\prime \pm \Delta^2 + \frac{1}{4} (\delta\phi)^2\right].$$

Now we discuss the above results. If the states prepared in the first step are perfect, then, in the second step, even if an inaccurate pulse amplitude (or duration) leads to the deviation of perfect $\pi$ pulses, purification of the right-handed molecules can also be effectively performed. (Here, we assume that equation (4), i.e., the CPT condition $\Omega_{13}(t)/\Omega_{23}(t) = i$ for left-handed molecules, should still be satisfied.) To show this, we let $\Delta = 0, \delta\phi = 0$ in equations (14)–(17) and the final populations in this case are $p_{1L,2}' \approx 1, p_3' \approx 0, p_{1L,2}' \approx \frac{1}{4} \Delta^2$ and $p_3' \approx 1 - \Delta^2$, respectively. This means that the left-handed molecules can be trapped in a superposition state of the two lower states, i.e., the CPT state $|\psi'_L\rangle$, while right-handed molecules can still be partially pumped to the higher state under imperfect $\pi$ pulses, and then purified by the following ionization process. Note that in this case both enantiomers cannot be perfectly purified, as not only left-handed molecules but also partial right-handed ones populate the two lower states ($p_{1L,2}' \approx \frac{1}{4} \Delta^2$). Thus, after ions formed by right-handed molecules are extracted by an electric field, the remainder is still the mixture of two enantiomers. But this is still meaningful, since in most cases only one enantiomer may produce the desired therapeutic (or biological) activities and thus we should extract merely the biologically beneficial chiral molecules from mixtures of enantiomers. To confirm the above analysis, figures 3(c) and (d) present a numerical simulation of the population dynamics for the left-handed and right-handed molecules initially prepared in the states $|1\rangle_L$ and $|1\rangle_R$ and driven by pulses with the Rabi frequencies $\Omega_{12}(t) = \frac{\sqrt{2}}{2}\exp[-(t - 3\tau)^2/\tau^2]$, $\Omega_{13}(t) = \frac{1}{\sqrt{2}}\exp[-(t - 9\tau)^2/(1.1\tau)^2]$ and $\Omega_{23}(t) = \frac{1}{\sqrt{2}}\exp[-(t - 9\tau)^2/(1.1\tau)^2]$, respectively. (Note that $\Omega_{13}(t)$ and $\Omega_{23}(t)$ can generate an effective $\pi$ rotation between the states $|\Phi\rangle_{LR}$ and $|3\rangle_{LR}$ with the Rabi frequency $\Omega(t) = \frac{\frac{\sqrt{2}}{2}}{\sqrt{2}}\exp[-(t - 9\tau)^2/(1.1\tau)^2]$, leading to a deviation of $\pi$ pulse: $\Delta' \approx 0.1 \times \frac{\pi}{2}$.) It can be seen from figures 3(c) and (d) that the left-handed molecules are finally populated in the two lower states $|1\rangle_L$ and $|2\rangle_L$ with $p_{1L}^\prime = p_{2L}^\prime = 1/2$, the right-handed molecules are mostly populated in the state $|3\rangle_R$ with $p_{3R}^\prime \approx 0.976$ and slightly populated in the states $|1\rangle_R$ and $|2\rangle_R$ with $p_{1R}^\prime \approx p_{2R}^\prime \approx 0.012$. For the more general case when all the applied Rabi frequencies in the two steps, either the intensity or the phase, are inaccurate, equations (14)–(17) give the final population of enantiomers theoretically. For a numerical simulation of population dynamics, we assume that the Rabi frequencies are designed as $\Omega_{12}(t) = \frac{\sqrt{2}}{2}\exp[-(t - 3\tau)^2/(1.1\tau)^2]$, $\Omega_{13}(t) = \frac{\sqrt{2}}{2}\exp[-(t - 9\tau)^2/(1.1\tau)^2] + i\frac{\sqrt{2}}{2}\frac{1}{\sqrt{2}}$ and $\Omega_{23}(t) = \frac{\sqrt{2}}{2}\exp[-(t - 9\tau)^2/(1.1\tau)^2]$, respectively. Again, note that $\Omega_{12}(t)$ can lead to a deviation of $\pi/2$ pulse $\Delta' \approx 0.1 \times \frac{\pi}{2}$; $\Omega_{13}(t)$ and $\Omega_{23}(t)$ can generate an effective rotation between the states $|\Phi\rangle_{LR}$ and $|3\rangle_{LR}$ with the Rabi frequency $\Omega(t) = \frac{\sqrt{2}}{2}\exp[-(t - 9\tau)^2/(1.1\tau)^2]$, leading to a phase imperfection $\delta\phi \approx 0.1 \times \frac{\pi}{2}$ and a deviation of the effective $\pi$ pulse $\Delta' \approx 0.1 \times \frac{\pi}{2}$. Under these pulses, the time evolution of the population of enantiomers is shown in figures 3(e) and (f). Our numerical calculation shows that after the pulses given above, the final populations are $p_{1L}^\prime + p_{2L}^\prime \approx 0.988$ and $p_{3R}^\prime \approx 0.964$, which is in accordance with theoretical evaluations given by equations (14)–(17). Obviously, these results show that if the applied pulses do not deviate very largely from perfect ones, after pulse operation, the left-handed molecules can be almost populated in the states $|1\rangle_L$ and $|2\rangle_L$, and the right-handed ones can be nearly populated in the state $|3\rangle_R$. Moreover, note that in practice the applied pulses can be more accurate than those used in our simulation and the influence of this inaccuracy is more less. Thus, even the given pulses are not so much perfect, the enantiomers can also be effectively prepared in different final states. Certainly, during the second driving process, the Rabi frequencies can also be designed as

$$\Omega_{13}(t) = -\Omega_{13}(t) = -i\Omega_{1}(t),$$

$$\Omega_{23}(t) = \Omega_{23}(t) = \Omega_{2}(t).$$

In this case, the right-handed molecules are pumped to the dark state $|\psi'_R\rangle$ and thus unchanged after the pulses, while the left-handed ones are pumped to the higher state. Thus, after pulse
operation, similar ionization and ions extraction processes can be implemented to separate the enantiomers.

In conclusion, we have introduced a two-step optical pulse method to achieve enantioseparations. In our protocol, the pulse processes are simplified by trapping one kind of chiral molecule in CPT states and the others is evolved to the highest levels for ionization. Compared with the previous three-step pulse method [14], our two-step operational approach is more robust in the presence of decoherence for fewer pulse steps, meaning shorter operation time. Additionally, even if the applied pulses are inaccurate, the enantiomers can also be effectively prepared in different final states and be separated. Finally, in our method, lower ionization energy is required, as the left(right)-handed molecules are prepared in their highest states.

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