Dynamic method to distinguish between left- and right-handed chiral molecules

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We study quantum systems with broken symmetry that can be modeled as cyclic three-level atoms with coexisting one- and two-photon transitions. They can be selectively optically excited to any state. As an example, we show that left- and right-handed chiral molecules starting in the same initial states can evolve into different final states by a purely dynamic transfer process. That means that left- and right-handed molecules can be distinguished purely dynamically.

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I. INTRODUCTION

In quantum systems with well-defined parities, one- and two-photon processes cannot coexist due to the electric-dipole selection rule [1]. However, this does not apply for quantum systems with a broken symmetry—e.g., chiral molecules whose symmetry is broken naturally, asymmetric quantum wells, or artificial "atoms" with broken symmetry, in which optical transitions will be allowed between any two levels. Recently, symmetry-broken artificial atoms [2] in a superconducting flux qubit circuit were investigated. By biasing the external magnetic flux Φ_e away from $\Phi_0/2$ ($\Phi_0 = h/2e$ is the magnetic flux quantum, h is the Planck constant, and e the electronic charge), the symmetries of both the potential and the interaction Hamiltonian can be broken. In this case, when only the lowest three levels are considered, the flux qubit circuit is a cyclic-type (or Δ-type) system, which is different from the usual Ξ-type (or ladder-type) system in which the optical dipole-selection rule does not allow a transition between the lowest and the uppermost of the three levels. By investigating the generalized stimulated Raman adiabatic passage (STIRAP [3]), one can achieve a pulse-phase-sensitive adiabatic manipulation of quantum states. The population can be cyclically transferred by controlling the amplitudes and/or phases of the coupling pulses. A cyclic system involving the coupling of nonclassical (quantized) optical fields has been investigated in Ref. [4]. Adiabatical (or dynamical) quantum information transfer between the collective excitations of a cyclic "atomic" ensemble and quantized optical fields has also been studied [5].

The existence of chiral molecules is one of the fundamental broken symmetries in nature. Chiral molecules can be modeled as being in a mirror-symmetric double-well potential [6,7]: left-handed states are in the left well and right-handed ones in the right. Strictly speaking, left- (right-) handed states in the left (right) wells are not the eigenstates of double-well potential due to the tunneling between the left and right wells. But the tunneling rates are usually very small, so left- (right-) handed states can be considered as stable eigenstates of chiral-molecule systems. Chiral purification and discrimination [8–12] of a mixture of chiral molecules are among the most important and difficult tasks in chemistry. The usual purification methods for chiral molecules are based on asymmetric synthesis—e.g., gas or liquid chromatographic methods [13]. Methods of achieving purifi-

cation solely by optical means have also been investigated theoretically [14–16]. Recently, Král *et al.* [17,18] proposed an optical-cyclic population-transfer scheme to distinguish mixed left- and right-handed molecules. Each kind of chiral molecule (left-handed or right-handed) can be modeled as a cyclic system if only the three lowest levels are considered. The left-handed cyclic system behaves like the right-handed one except for the intrinsically-different total phases of the three Rabi frequencies if three transitions are coupled to three optical fields, respectively. The idea was to optically transfer chiral molecules which are in their initial respective ground states to final levels at different energies. This population transfer was achieved by adiabatical (or diabatical) optically coupled processes.

In another development, there has been considerable interest in implementing pseudospin-dependent optically induced gauge potentials for cold atoms to achieve a spatial separation of pseudospin states [19,20]. Based on this scheme, we recently considered the consequences of the induced gauge potential in systems of cold chiral molecules that manifest themselves as a generalized Stern-Gerlach effect [21], where the orbital motion of mixed chiral molecules will be chirality dependent and pseudospin dependent. Thus, it can be used to distinguish molecules with different chiralities, suggesting a discrimination method to separate chiral mixtures.

In this paper, we will use a dynamical (rotation) method to transfer the states of cyclic three-level systems with broken symmetry by applying ultrashort π or $\pm\pi/2$ optical pulses. Interestingly, we can distinguish mixed left- and right-handed molecules (in their respective ground states) by dynamically driving them to different-energy final states.

II. POPULATION TRANSFER VIA DYNAMIC PROCESSES

The general cyclic three-level system coupled with three classical optical fields, respectively, can be described by the Hamiltonian [17] in the rotating-wave approximation ($\hbar = 1$)

$$H_{ori} = \sum_{j=1}^{3} \omega_j |j\rangle + \sum_{i>j=1}^{3} \left[\Omega_{ij}(t) e^{-i\omega_{ij}t} |i\rangle\langle j| + \text{H.c.} \right], \quad (1)$$

where ω_j are the energies of the states $|j\rangle$, ω_{ij} are the frequencies of the optical fields coupling to the transition
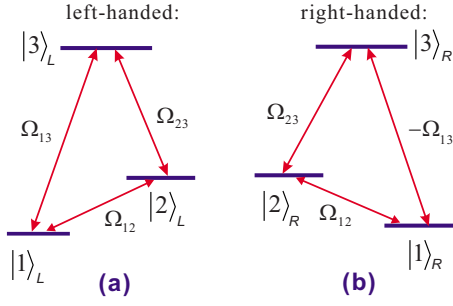
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FIG. 1. (Color online) Model of left- (a) and right- (b) handed chiral molecules by a three-level Δ-type (or cyclic) system, which is resonantly coupled to three classic optical fields with Rabi frequencies Ω_{12}, Ω_{23}, and $\pm\Omega_{13}$.

$|i\rangle \leftrightarrow |j\rangle$, and $\Omega_{ij}(t) = \vec{\mu}_{ij} \cdot \vec{E}_{ij}$ are the Rabi frequencies which can be controlled by varying the field strength $\vec{E}_{ij}$; $\vec{\mu}_{ij}$ is the dipole matrix element between the states $|i\rangle$ and $|j\rangle$. The analytic instantaneous eigenfrequencies and eigenfunctions have been evaluated in Refs. [2,17]. At resonance $\omega_{ij} \equiv \omega_i - \omega_j$, the above Hamiltonian can be rewritten in the interaction picture as

$$H = \sum_{i>j=1}^{3} \Omega_{ij}(t)|i\rangle\langle j| + \text{H.c.} \qquad (2)$$

The goal of this paper is to present a purely dynamic method to separate left- and right-handed chiral molecules. If left- and right-handed three-level cyclic molecules are driven by three optical fields, one or all of the three Rabi frequencies $\Omega_{ij}(t)$ for the two kinds of chiral molecules differ by a sign [17,18]. We will specify our model by choosing the coupling strengths (that is, Rabi frequencies) of the left- and right-handed molecules as $\Omega_{ij}^{L}(t) \equiv \Omega_{ij}(t)$ and $\Omega_{13}^{R}(t) \equiv -\Omega_{13}(t)$, $\Omega_{12}^{R}(t) \equiv \Omega_{12}(t)$, and $\Omega_{23}^{R}(t) \equiv \Omega_{23}(t)$ (see Fig. 1). Here, the superscripts L (R) refer to left-handed (right-handed) molecules.

We now consider an ensemble of left- and right-handed molecules prepared in their ground states $|1\rangle_L$ and $|1\rangle_R$, respectively. We aim to distinguish the two kinds of molecules by transferring them to different-energy final states. Our separation protocol consists of the following steps (see Fig. 2).

Step I. At time $t=0$, we start with a pump pulse $\Omega_{13}(t)$ for the left-handed molecules. The corresponding Hamiltonian will reduce to

$$H_L^I = \Omega_{13}(t)|1\rangle_{LL}\langle 3| + \text{H.c.} \qquad (3)$$

Here we control the pulse to cause a $\pi/2$ rotation [22] for the left-handed molecules,

$$|\psi_0\rangle_L \equiv |1\rangle_L \rightarrow |\psi_I\rangle_L \equiv \frac{1}{\sqrt{2}}(|1\rangle_L - i|3\rangle_L). \qquad (4)$$

For the right-handed ones, the Rabi frequency is $-\Omega_{13}(t)$, which leads to a $-\pi/2$ rotation
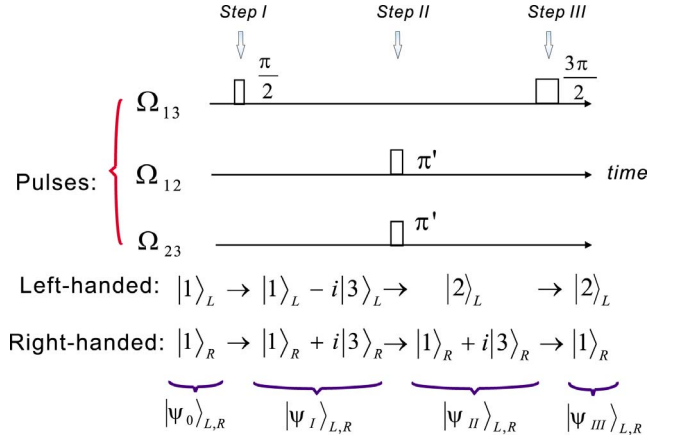

FIG. 2. (Color online) Schematic representation of the three steps to discriminate two kinds of chiral molecules. All the operations consist of simple $\pm\pi/2$ and π rotation pulses of three optical coupling strengths (Rabi frequencies). Here, the notation π' is used to indicate a π rotation pulse for the effective Rabi frequency $\Omega_{\text{eff}}(t)$ [$=\sqrt{2}|\Omega_{12}(t)| = \sqrt{2}|\Omega_{23}(t)| = \sqrt{2}\Omega_0(t)$], and *not* for the Rabi frequencies $\Omega_{12}(t)$ and $\Omega_{23}(t)$.

$$|\psi_0\rangle_R \equiv |1\rangle_R \rightarrow |\psi_I\rangle_R \equiv \frac{1}{\sqrt{2}}(|1\rangle_R + i|3\rangle_R), \qquad (5)$$

with the corresponding Hamiltonian

$$H_R^I = -\Omega_{13}(t)|1\rangle_{RR}\langle 3| + \text{H.c.} \qquad (6)$$

Step II. Now we keep $\Omega_{13}(t) \equiv 0$ and add two pump pulses of $\Omega_{12}(t)$ and $\Omega_{23}(t)$, which satisfy

$$\Omega_{12}(t) = i|\Omega_{12}(t)| \equiv i\Omega_0(t) = i\Omega_{23}(t). \qquad (7)$$

Hence, the Hamiltonian (2) for the left-handed molecules reads

$$H_L^{II} = \Omega_{\text{eff}}(t)(|B\rangle_{LL}\langle 2| + \text{H.c.}), \qquad (8)$$

where $|B\rangle_L = (i|1\rangle_L + |3\rangle_L)/\sqrt{2}$ and $\Omega_{\text{eff}}(t) = \sqrt{2}\Omega_0(t)$. The instantaneous eigenfunctions for Eq. (8) are

$$|E_0\rangle_L = \frac{1}{\sqrt{2}}(|1\rangle_L + i|3\rangle_L),$$

$$|E_{\pm}\rangle_L = \frac{1}{\sqrt{2}}(|2\rangle_L \pm |B\rangle_L), \qquad (9)$$

with the corresponding eigenvalues

$$E_0 = 0, \quad E_{\pm} = \pm \Omega_{\text{eff}}(t). \qquad (10)$$

Hence, for the left-handed molecule, the corresponding time evolution of the state is given as

$$|\psi_{II}\rangle_L = \exp\left(-i \int_0^t H_L^{II}(t')dt'\right)|\psi_I\rangle_L$$

$$= \frac{-i}{\sqrt{2}}(e^{-i\eta(t)}|E_+\rangle_L - e^{i\eta(t)}|E_-\rangle_L), \quad (11)$$

where $\eta(t) := \int_0^t \Omega_{eff}(t')dt'$. If $\Omega_{eff}(t)$ is chosen to cause a rotation by π corresponding to the transition $|2\rangle_L \leftrightarrow |B\rangle_L$—that is, $\eta(t) = \pi/2$—the evolved state is

$$|\psi_{II}\rangle_L = -|2\rangle_L. \quad (12)$$

The same treatment applies to the right-handed molecules by replacing L by R in Eqs. (8) and (9). Since the state $|\psi_I\rangle_R = (|1\rangle_R + i|3\rangle_R)/\sqrt{2}$ is always the dark state for the Hamiltonian $H_R^{II} = \Omega_{eff}(t)(|B\rangle_{RR}\langle 2| + \text{H.c.})$, it is invariant during the π rotation in this step. Thus, we obtain the following state after step II:

$$|\psi_{II}\rangle_R \equiv |\psi_I\rangle_R = \frac{1}{\sqrt{2}}(|1\rangle_R + i|3\rangle_R) \quad (13)$$

for the right-handed molecules.

Step III. Now we keep $\Omega_{12}(t) = \Omega_{23}(t) \equiv 0$ and apply the pump pulse $\Omega_{13}(t)$ leading to a $3\pi/2$ rotation for the left-handed molecules [the corresponding Rabi frequency is $-\Omega_{13}(t)$ with a $-3\pi/2$ (or $\pi/2$) rotation for the right-handed ones]. The left-handed molecular state $|2\rangle_L$ remains unchanged:

$$|\psi_{III}\rangle_L = |\psi_{II}\rangle_L = -|2\rangle_L. \quad (14)$$

On the other hand, the $-3\pi/2$ rotation pulse acting on the right-handed molecules will transfer the state $|\psi_{II}\rangle_R$ to the final state:

$$|\psi_{III}\rangle_R = |1\rangle_R. \quad (15)$$

Here, the corresponding Hamiltonians for the chiral molecules are again given by Eqs. (3) and (6), respectively.

The above protocol, which includes several simple ultrashort rotations, will bring the initial state $|1\rangle_L \rightarrow |2\rangle_L$ for the left-handed molecules and $|1\rangle_R \rightarrow |1\rangle_R$ for the right-handed ones. The fact that different-handed chiral molecules are transferred to different long-lived states means perfect discrimination of both kinds of chiral molecules in our idealized treatment.

Figure 3 shows an illustration of this separation procedure. Initially, all the molecules are assumed to be in the ground state $|1\rangle_{L,R}$ as shown in Fig. 3(a). By using simple optical pulses—i.e., switching on and off the optical fields as shown in Fig. 2—the two kinds of chiral molecules are dynamically transferred from the initial state $|1\rangle_{L,R}$ to the final state $|2\rangle_L$ and $|1\rangle_R$, respectively [see Fig. 3(b)]. These different states may be separated [see Fig. 3(c)] using a variety of energy-dependent processes, such as ionization, followed by extraction of the ions by an electric field as suggested in Ref. [17].

The scheme proposed here is different from the generalized Stern-Gerlach effect [21] in the following respects: (i) There is no need to invoke the spatial motion of the molecules in the scheme presented here; it is enough to consider
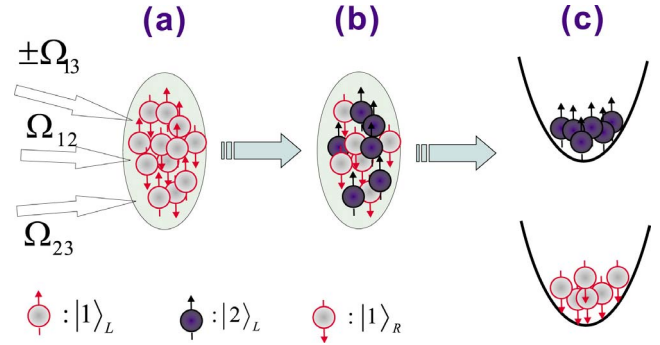

FIG. 3. (Color online) Illustration of the separation procedure. (a) Initially, all the (oriented) chiral molecules are prepared in the ground states $|1\rangle$ before the coupling to the optical fields (here the optical fields can be coplanar or not). The labels of spin-up (-down) refer to the left- (right-) handed molecules. (b) After driving the optical pulses in the protocol as shown in Fig. 2, the chiral molecules are dynamically transferred to the final states $|2\rangle_L$ and $|1\rangle_R$, respectively. The dark (bright) spheres indicate the states $|2\rangle$ ($|1\rangle$). (c) The different-handed chiral molecules may now be separated—e.g., by ionization or choosing different trapping potentials for different energy levels.

their internal dynamics. (ii) The internal degree of freedom of a three-level system is reduced to the lower two (pseudospin) states in Ref. [21] by assuming a large detuning. Here, we discuss the molecular dynamics in the space of three levels with all the optical coupling resonant to the corresponding transition. (iii) Different chiral molecules can be separated spatially; here, we only focus on how to distinguish different chiral molecules according to the different final states as in Refs. [17,18].

The present protocol is also different from the methods described in Refs. [17,18], where molecules with different chirality are distinguished by adiabatical processes via controlling three overlapping optical fields. The dynamical rotation method proposed here provides another possibility to distinguish mixed chiral molecules by using several simple optical ultrashort pulses. In contrast to the scheme described in Ref. [18], we assume the molecules to be pre-oriented (similar to Refs. [17,21]) in order to ensure that the Rabi frequencies are identical for all the molecules in the mixture (up to a phase factor) when coupling to a same optical field.

In the present separation scheme as well as similar ones [17,18,21], the molecular temperature is assumed to be low enough such that the molecules are prepared in the ground state initially. We neglect finite-temperature effects and molecular interactions.

In the protocol described above, all three kinds of optical fields couple resonantly to the molecular transitions. That means that the optical fields satisfy the energy conservation condition $\omega_{12} + \omega_{23} = \omega_{13}$. This resembles sum-frequency generation in nonlinear media [23], which requires energy conservation as well as momentum conservation (along a certain direction). Sum-frequency generation is one of the techniques used to probe (but not separate) molecular chirality [24]. The separation protocol described in our paper is not related to sum-frequency generation and is not constrained

by the momentum conservation of optical wave-vectors (that is why the three optical fields can be coplanar or not).

Recently, many studies about preparing, measuring, and teleporting superpositions of chiral states [25] have appeared in the literature. In these works, superposition states are obtained by involving a symmetric or antisymmetric higher excited state which can couple to the left-handed or right-handed states by optical fields. In this paper, we aim to separate mixtures of left-handed and right-handed chiral molecules. So the external excited state is not introduced and superpositions of chiral states are not considered here.

Decoherence processes are the biggest obstacle for any quantum-state-transfer operation. Due to the fact that our protocol only uses dynamic ultrashort-pulse operations and does not require adiabaticity assumptions, our method will work faster and make decoherence effects less important.

III. CONCLUSION

In conclusion, we have presented a protocol to separate left- and right-handed molecules. This protocol, which con-

sists of several simple dynamical rotation operations of optical pulses, can be implemented on a short time scale compared with the decoherence time due to spontaneous emission. We would like to remark that all three kinds of optical couplings have to be used (though not at the same time) during the rotation operations in this separation protocol. Physically, this is because the two kinds of chiral molecules can be distinguished only by the total phase of the three Rabi frequencies (which differ by π). If only two kinds of optical couplings are used, the molecular system will reduce to the V-, Λ-, or ladder-type three-level system, which cannot be used to distinguish different chiralities.

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