Cyclic Population Transfer in Quantum Systems with Broken Symmetry

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(Received 19 April 2001; published 12 October 2001)

We show that quantum systems with broken symmetry can be selectively excited due to the coexistence of one- and two-photon transitions between the *same* states. Discrimination between two mirror-symmetric quantum wells or left- and right-handed chiral molecules can be accomplished by a "cyclic population transfer" process, in which one optically couples three system states $|1\rangle \leftrightarrow |2\rangle \leftrightarrow |3\rangle \leftrightarrow |1\rangle$, and completely transfers population from state $|1\rangle$ to state $|2\rangle$ and $|3\rangle_M$ (i.e., state $|3\rangle$ of the *mirror imaged* system) or state $|3\rangle$ and $|2\rangle_M$, depending on the laser phases.

DOI: 10.1103/PhysRevLett.87.183002 PACS numbers: 33.15.Bh, 33.80.Be, 42.50.Hz, 78.67.–n

Adiabatic passage phenomena [1] are known to cause complete population transfers between quantum states. In the particular realization of adiabatic passage (AP), called stimulated rapid adiabatic passage (STIRAP) [2,3], population in state $|1\rangle$ can be transferred to state $|3\rangle$, by a "counterintuitive" sequence of two one-photon transitions using an intermediate state $|2\rangle$. The method has been applied to atomic and molecular systems [2,3], as well as to quantum dots [4].

Ordinary STIRAP is sensitive only to the energy levels and the *magnitudes* of transition-dipole coupling matrix elements between them. These quantities are identical for a chiral system and its mirror image (such pairs are called "enantiomers" [5]). Its insensitivity to the *phase* of the transition-dipole matrix elements renders STIRAP, and ordinary weak-field absorption [6], incapable of selecting between enantiomers. Recently [7], we have shown, however, that this objective can be realized by other (phase sensitive) optical processes in the weak-field regime.

In this Letter, we demonstrate that precisely the *lack of inversion center,* which characterizes chiral and other broken-symmetry systems, allows us to combine the weak-field one- and two-photon method [8–11] with the strong-field STIRAP, to render a phase-sensitive AP method. In this "cyclic population transfer" method (CPT), one closes the STIRAP two-photon process $|1\rangle \leftrightarrow |2\rangle \leftrightarrow |3\rangle$ by a one-photon process $|1\rangle \leftrightarrow |3\rangle$. One-photon and two-photon processes cannot coexist in the presence of an inversion center, where all states have a *well-defined parity*, because a one-photon absorption (emission) between nondegenerate states $|1\rangle$ and $|3\rangle$, requires that these states have opposite parities, whereas a two-photon process requires that these states have the same parity.

Contrary to systems possessing an inversion center, in which the interference between weak-field one- and two-photon processes in a continuum leads to a phase control of *differential* properties, e.g., current directionality [8–11], we show that the CPT process of broken symmetry systems allows us to control *integral* properties as well. A prime example is the control of the complete population, transferred to excited states of two enantiomers.

Specific examples for the use of CPT are illustrated in Fig. 1 (upper plot). One example deals with a pair of asymmetric quantum wells, one being the mirror image of the other. Another example consists of two heteronuclear molecules aligned in an external dc electric field [12], to break their rotational symmetry, or a mixture of left- and right-handed enantiomeric molecules [7].

In the setup of Fig. 1 (lower plot), we consider operating on states $|i\rangle$ and their mirror images $|i\rangle_M$ by three pulses in a "counterintuitive" order [2,3], i.e., *two* "pump" pulses with Rabi frequencies $\Omega_{12}(t)$ and $\Omega_{13}(t)$, which follow a "dump" pulse $\Omega_{23}(t)$. The Rabi frequencies are defined as $\Omega_{ij}(t) \equiv \mu_{ij}\mathcal{E}_{ij}(t)/\hbar = |\Omega_{ij}(t)|e^{i\phi_{ij}} = \Omega^*_{ji}(t)$, where μ_{ij} and $\mathcal{E}_{ij}(t)$ are, respectively, the transition dipoles and the envelopes of electric fields, of central frequencies ω_{ij}, operating between states $i \neq j$ $(i, j = 1, 2, 3)$. If we symmetrically detune the pulse center frequencies, as

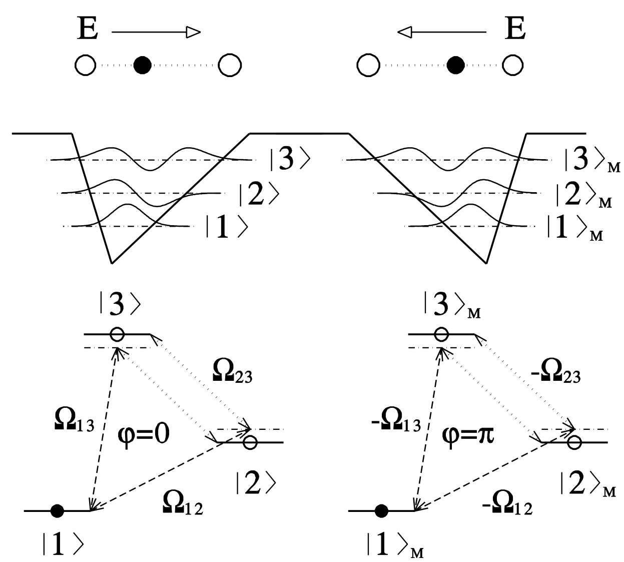

FIG. 1. (Upper plot) An asymmetric quantum well and its mirror image. Also shown are two field-oriented heteronuclear molecules. (Lower plot) Illustration of the three pulses used in these CPT systems. The two systems can be discriminated by their different matter-radiation phases φ.

shown in Fig. 1, we satisfy the $|1\rangle \leftrightarrow |2\rangle \leftrightarrow |3\rangle$ and $|1\rangle \leftrightarrow |3\rangle \leftrightarrow |2\rangle$ two-photon resonance condition, while keeping the one-photon processes, $|1\rangle \leftrightarrow |3\rangle$ and $|1\rangle \leftrightarrow |2\rangle$, off resonance. As a result, the loop formed by the three transitions is not resonantly closed. Therefore, the one and two-photon processes interfere only at isolated points in time, when the pulses are on.

We now solve explicitly the problem by first writing the CPT (radiation + matter) Hamiltonian in the rotating wave approximation as

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

where ω_j are the energies of the states $|j\rangle$, and atomic units ($\hbar = 1$) are used throughout. The system wave function can be written as

$$|\psi(t)\rangle = \sum_{n=1}^{3} c_n(t) e^{-i\omega_n t} |n\rangle, \tag{1}$$

where $\mathbf{c} = (c_1, c_2, c_3)^{\mathsf{T}}$, the column vector of the slow varying coefficients, can be evaluated from the Schrödinger equation

$$\dot{\mathbf{c}}(t) = -i\mathsf{H}(t) \cdot \mathbf{c}(t) \tag{2}$$

with $\mathsf{H}(t)$, the effective Hamiltonian matrix, given as

$$\mathsf{H} = \begin{bmatrix} 0 & \Omega_{12}^{*} e^{i\Delta_{12}t} & \Omega_{13}^{*} e^{i\Delta_{13}t} \\ \Omega_{12} e^{-i\Delta_{12}t} & 0 & \Omega_{23}^{*} e^{i\Delta_{23}t} \\ \Omega_{13} e^{-i\Delta_{13}t} & \Omega_{23}^{*} e^{i\Delta_{23}t} & 0 \end{bmatrix}. \tag{3}$$

Here we have omitted, for brevity, writing explicitly the time dependence of $\Omega_{ij}(t)$, and the detunings are defined as $\Delta_{ij} = \omega_i - \omega_j + \omega_{ij} = -\Delta_{ji}$.

In contrast to ordinary STIRAP, unless $\Sigma \equiv \Delta_{12} + \Delta_{23} + \Delta_{31} = 0$, it is not possible to transform away the rapidly oscillating $e^{-i\Delta_{ij}t}$ components from the CPT Hamiltonian [Eq. (3)]. Therefore, the system phase factor varies as ($e^{-i\Sigma t}$) during the time when the three pulses overlap. As a result, in CPT, unless $\Sigma = 0$, null states (i.e., states with zero eigenvalue) disappear when the pulses overlap. Moreover, due to nonadiabatic couplings, the population does not follow a single eigenstate during the entire time evolution, migrating at the near-crossing region from the initially occupied null state.

We can quantify the above statements by examining the eigenvalues of the Hamiltonian of Eq. (3), given as

$$E_2 = \frac{2^{1/3}a}{3c} + \frac{c}{3 2^{1/3}}, \qquad E_{1,3} = \frac{-(1 \pm i\sqrt{3})a}{3 2^{2/3} c} - \frac{(1 \mp i\sqrt{3})c}{6 2^{1/3}}, \tag{4}$$

where

$$a = 3(|\Omega_{12}|^2 + |\Omega_{23}|^2 + |\Omega_{31}|^2),$$
$$b = 3^3 \, \mathrm{Det}(\mathsf{H}) = 3^3 2 \, \mathrm{Re}\mathcal{O},$$

and

$$c = [b + \sqrt{b^2 + 4(-a)^3}\,]^{1/3},$$

with $\mathcal{O} = \Omega_{12}\Omega_{23}\Omega_{31} e^{-i\Sigma t}$.

We see that the three eigenvalues depend only on the *overall phase* of $\mathcal{O}$. This phase is composed of a *time-independent* part $\varphi \equiv \phi_{12} + \phi_{23} + \phi_{31}$, of the product of the Rabi frequencies, and a *time-dependent* part Σt. Therefore, from Eq. (4), it follows that if $\varphi = \pm\pi/2$ and $\Sigma = 0$, we have $b = 0$, hence, $c = i2^{1/3}a^{1/2}$ and $E_2 = 0$.

In Fig. 2 we present the time dependence of the eigenvalues $E_i(t)$ ($i = 1, 2, 3$) for three Gaussian pulses parametrized as $|\Omega_{23}(t)| = \Omega_{\max} \exp[-t^2/\tau^2]$, $|\Omega_{12}(t)| = 0.7\Omega_{\max} \exp[-(t - t_2)^2/\tau^2]$, and $|\Omega_{13}(t)| = 0.7\Omega_{\max} \exp[-(t - t_3)^2/\tau^2]$, with $\Omega_{\max} = 30/\tau$, where τ is the pulse width. The pulse delays are $t_3 = t_2 = 2\tau$ and the detunings, chosen to give maximal selectivity, are $\Delta_{12} = -\Delta_{13} = -\Delta_{23} = 0.08/\tau$. The eigenvalues are presented for the phases $\varphi = 0.235\pi$ (see Fig. 4) and $\varphi = (0.235 - 0.5)\pi$.

For the problem defined by the parameters of Fig. 2, $(|c_1|, |c_2|, |c_3|)$, the vector of magnitudes of the expansion coefficients of the $|E_i\rangle$ eigenvectors in the "bare" basis, starts in the remote past ($t \to -\infty$) as $(1, 0, 0)$ for $|E_2\rangle$, and as $(0, 1, 1)/\sqrt{2}$ for $|E_1\rangle$ and $|E_3\rangle$. Since the evolution starts with bare state $|1\rangle$, only the $|E_2\rangle$ eigenstate gets initially populated. At the end of the process, we have that $(|c_1|, |c_2|, |c_3|) \overset{t\to\infty}{\longrightarrow} (0, 1, 1)/\sqrt{2}$ for $|E_2\rangle$, and $\overset{t\to\infty}{\longrightarrow} (\sqrt{2}, 1, 1)/2$ for $|E_1\rangle, |E_3\rangle$.

Figure 2 clearly shows that the system evolution is governed by the interference between $|1\rangle \to |3\rangle \to |2\rangle$ and $|1\rangle \to |2\rangle \to |3\rangle$ two-photon processes, which are arranged in Fig. 1 with a "clockwise" and "counterclockwise" sequence of involved levels. This interference

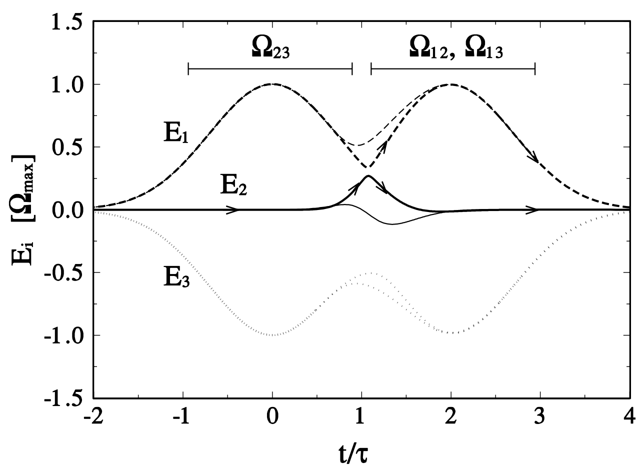

FIG. 2. The three dressed eigenvalues $E_i(t)$ at two different phases. The solution for $\varphi = 0.235\pi$ and $\varphi = (0.235 + 0.5)\pi$ is plotted by thick and thin lines, respectively. An initial population at state $|1\rangle$ stays on the null state $|E_2(t)\rangle$ with $E_2(t) \approx 0$ up to the avoided crossing region where the population becomes shared with the eigenstate $|E_1(t)\rangle$ or $|E_3(t)\rangle$, depending on the phase φ. The horizontal short lines denote the approximate times of action of the Rabi frequencies Ω_{ij}.

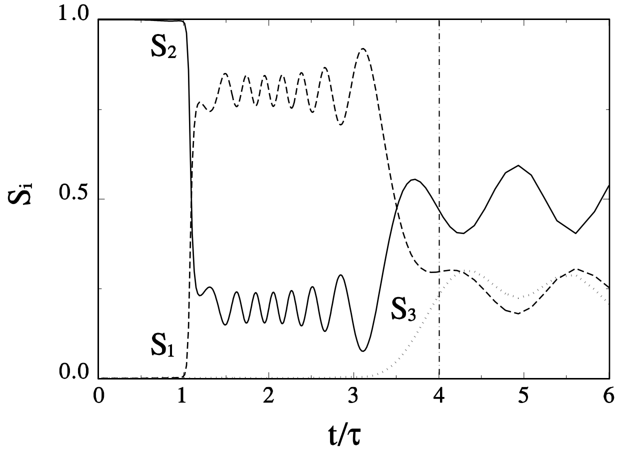

FIG. 3. The populations, given as $S_i(t) \equiv |\langle E_i(t)|\psi(t)\rangle|^2$, of the field-dressed states, given that $|\psi(t=0)\rangle = |1\rangle$ and $\varphi = 0.235\pi$. All other parameters are as in Fig. 2. The thin vertical (— · — · — ·) line points at the time after which the population in the bare states $|i\rangle$ roughly cease to vary.

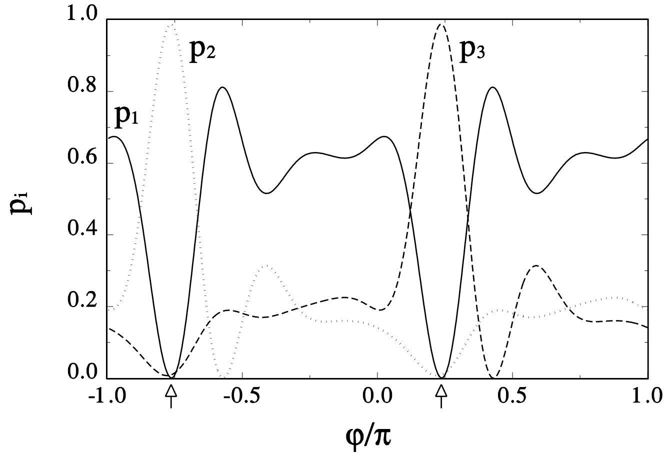

FIG. 4. Dependence of p_i, the final populations of the bare states $|i\rangle$ on the phase φ. The two vertical arrows show the phases for the best separation of the chiral systems, where the population is transferred from state $|1\rangle$ to states $|2\rangle$ or $|3\rangle$.

results in the appearance of an avoided crossing between the $E_2(t)$ eigenvalue and (depending on the phase φ) either the $E_1(t)$ or the $E_3(t)$ eigenvalue. In the crossing region, the adiabatic description ceases to be valid, and the system populates a *superposition state* $\alpha_2|E_2\rangle + \alpha_i|E_i\rangle$ ($i = 1$ or $i = 3$).

Figure 3 displays the evolution of the populations $S_i(t) \equiv |\langle E_i(t)|\psi(t)\rangle|^2$ of the field-dressed states, having started with $|\psi(t=0)\rangle = |1\rangle$. The parameters are as in Fig. 2, with φ being confined to the 0.235π value. We see that the eigenstate $|E_2\rangle$ is populated exclusively until the avoided crossing region, where the system goes to the state $\alpha_2|E_2\rangle + \alpha_1|E_1\rangle$. As the pulses wane and all $\Omega_{ij}(t) \to 0$, *nonadiabatic* processes populate also the $|E_3\rangle$ state. The populations of the $|E_1\rangle$ and $|E_3\rangle$ states have roughly the same magnitudes $S_1 \approx S_3$ at the end of the process, as expected from the roughly equal final values of the $|c_1|, |c_2|, |c_3|$ coefficients shown above. Hence, by varying φ and Σ we can adjust the α_i coefficients such that $\sum_i \alpha_i|E_i\rangle \overset{t\to\infty}{\to} |2\rangle$ or $|3\rangle$.

An example of the degree of control attainable in this manner is given in Fig. 4, where we display the phase dependence of the final populations p_i of the bare states $|i\rangle$, using the parameters of Figs. 2–3. The main feature of Fig. 4 is that the role of state $|2\rangle$ vs state $|3\rangle$ is *reversed* as we translate the phase φ by π. This feature serves, as discussed below, to establish the discrimination between left-handed and right-handed chiral system.

The calculations of Fig. 4 show enhanced sensitivity of the final populations p_i on φ at small detunings Δ_{ij}. The population transfer can be made essentially complete by choosing $\varphi \approx 0.235\pi$ (denoted by a small arrow at the bottom of Fig. 4). In that case, 99% of the population is transferred from state $|1\rangle$ to state $|3\rangle$. As the phase φ is shifted by π, the system switches over, with the same efficiency, to the $|1\rangle \to |2\rangle$ population transfer process.

A complementary view of the dynamics is provided by examining the two Bloch vectors with components $[|c_1|^2 - |c_i|^2, \mathrm{Re}(c_1^* c_i), \mathrm{Im}(c_1^* c_i)]$ ($i = 2,3$), shown in Fig. 5. Starting from the initial position of $(1,0,0)$, both vectors leave the avoided-crossing region in a superposition state $\alpha_2|E_2\rangle + \alpha_1|E_1\rangle$, where they oscillate with the Rabi frequency $|\Omega_{12}| = |\Omega_{13}|$. The final populations p_i of the bare states $|i\rangle$ are determined by the *second mixing* of the $|E_i\rangle$ states, during the waning of the pulses. This nonadiabatic process reduces the population to the approximate final state $|3\rangle$, so the two Bloch vectors end in the positions $(-1,0,0)$ and $(0,0,0)$.

The phase dependence of CPT can be used to discriminate between left- and right-handed chiral systems. Denoting by $|i^+\rangle$ (formerly $|i\rangle$) a given symmetry-broken state and by $|i^-\rangle$ (formerly $|i\rangle_M$) its mirror image, we can write these states in terms of symmetric $|S_i\rangle$ and antisymmetric $|A_i\rangle$ states of the two systems as [5,7], $|i^\pm\rangle = s_i|S_i\rangle \pm a_i|A_i\rangle$. Because dipole moments can only connect states of opposite parity, we obtain that the Rabi frequencies for transition between different symmetry-broken states $|i^\pm\rangle$ and $|j^\pm\rangle$ are given as $\Omega_{ij}^\pm = \pm[s_i^* a_j\langle S_i|\mu|A_j\rangle + a_i^* s_j\langle A_i|\mu|S_j\rangle]\mathcal{E}_{ij}$. We see that the Rabi frequencies between any pair of left- and right-handed states differ by a sign, i.e., a phase factor of π. Since in the CPT processes the two enantiomers are influenced by the phase $\varphi^\pm$ of the products $\Omega_{12}^\pm\Omega_{23}^\pm\Omega_{31}^\pm$, we always have that $\varphi^- - \varphi^+ = \pi$. This property is *invariant* to any arbitrary phase change in the individual wave functions of the states $|i^\pm\rangle$.

It therefore follows from Fig. 4, where a change in π of the phase φ is seen to switch the population-transfer process from $|1\rangle \to |2\rangle$ to $|1\rangle \to |3\rangle$, and vice versa, that we can affect the transfer of population in one chiral system relative to its mirror image. Because the overall *material phase* $\varphi_s^\pm$ of the product of the dipole matrix elements $\mu_{12}^\pm\mu_{23}^\pm\mu_{31}^\pm$ is a fixed quantity ($\varphi_s^- - \varphi_s^+ = \pi$),

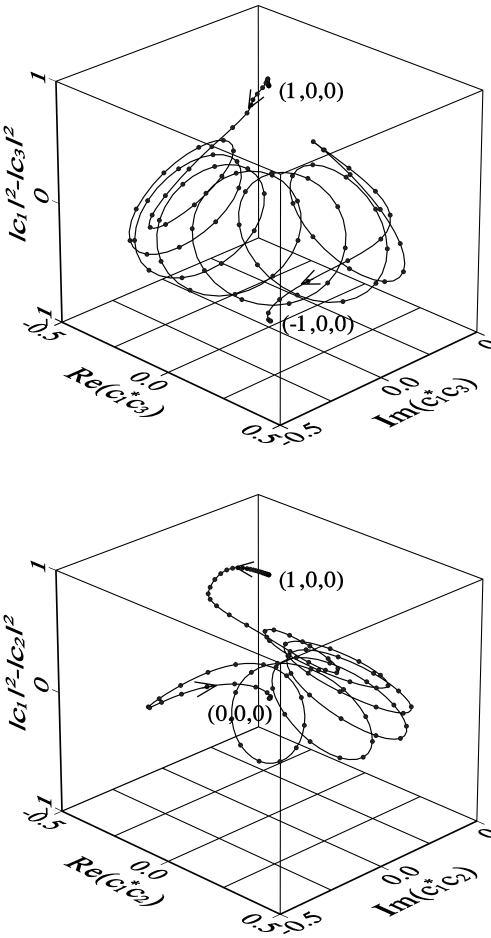

FIG. 5. The Bloch vector $[|c_1|^2 - |c_i|^2, \mathrm{Re}(c_1^* c_i), \mathrm{Im}(c_1^* c_i)]$ evolution, where $i = 3$ and $i = 2$ holds for the top and bottom plot, respectively. Population starting in the initial state $|1\rangle$ is clearly transferred to the final state $|3\rangle$.

and $\varphi^{\pm} = \varphi_s^{\pm} + \varphi_f$, it is the overall phase φ_f of the *three laser fields* $\mathcal{E}_{ij}$ which acts as the laboratory knob allowing us to determines which population-transfer process is experienced by each of the two enantiomers.

The ability of CPT to separate two enantiomers also depends on the individual detuning parameters Δ_{ij} and on the related dynamical phase $2\Sigma\tau$. At resonance $\Delta_{ij} = 0$ and $\varphi = \pm\pi/2$, the exact null eigenstate $|E_2(t)\rangle$ gives a complete adiabatic population transfer from state $|1\rangle$ to a combination of states $|2\rangle$ and $|3\rangle$. In that case, the p_2/p_3 branching ratio of the final populations is given, as in the double STIRAP case [14,15], by the $|\Omega_{12}/\Omega_{13}|^2$ ratio and no enantiomeric selectivity is then possible. In general, the strong-field excitation of enantiomers can be achieved only in *nonadiabatic* CPT regimes.

Once each enantiomer has been excited to a different state ($|2\rangle$ or $|3\rangle$), the pair can be physically separated using a variety of energy-dependent processes, such as ionization, followed by ions extraction by an electric field. If we execute the CPT excitation in the IR range and ionize the chosen enantiomer after only a few nsec delay, losses from fluorescence, whose typical lifetimes are in the msec range, are expected to be minimal.

In summary, we have shown that cyclic population transfer (CPT) in a three level system ($|1\rangle, |2\rangle, |3\rangle$) can discriminate between two molecules or two nanosystems lacking a center of inversion. This *phase-sensitive* scheme is based on the coexistence of one- and two-photon processes operating between the same initial and final states, leading to interferences between the $|1\rangle \rightarrow |3\rangle \rightarrow |2\rangle$, "clockwise" and the $|1\rangle \rightarrow |2\rangle \rightarrow |3\rangle$, "counterclockwise" optical processes. The interference, which depends on the (laboratory controlled) overall phase of the three laser fields involved, results in a selective excitation of one asymmetric system relative to its mirror image. Following such a selective excitation, a number of simple, energetically dependent, physical separation schemes, such as ionization, followed by ions extraction by an electric field, can be employed.

We acknowledge discussions with J. Fiurášek, and support from the Minerva Foundation, GIF, the EU IHP programme HPRN-CT-1999-00129, and the U.S. Office of Naval Research.

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