



Geometric phase and parity-violating energy difference locking of chiral molecules

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ARTICLE INFO

Article history:

Received 13 September 2011

In final form 8 December 2011

Available online 14 December 2011

ABSTRACT

Geometric phases within a canonical formulation of chiral molecules are analyzed paying special attention to the fundamental role played by the parity violating energy difference. We study the Hamiltonian dynamics in terms of canonically conjugate variables, showing how parity-violating energy difference could be locked (PVED-locking) by means of a circularly polarized electric field. Signatures of this locking are predicted to occur both in the geometric phase and in the interference between chiral states.

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1. Introduction

The still elusive experimental detection of electroweak symmetry-breaking in chiral molecules is one of the most fascinating problems which links very detailed theoretical and experimental studies devoted to measure the parity violating energy difference (PVED) between the two enantiomers of chiral molecules (a consequence of the theory of electroweak interactions). This PVED is estimated to be between 10^{-13} and 10^{-21} eV [1,2] but no conclusive energy difference has been reported up to date. In particular, high-resolution laser spectroscopy of bromochlorofluoromethane (CHBrClF) has been extensively studied [3] but no unambiguous observation has been made so far up to a precision of 10^{-14} in the relative shift of the hyperfine component of the C–F stretching fundamental band of the two enantiomers (see [3] and references therein). Based on the observation of quantum beats in the electroweak optical activity of chiral molecules, several experimental techniques have been proposed for the observation of parity violation in molecular systems such as, for example, rovibrational [4], electronic [5,6], Mossbauer [7] and NMR spectroscopies [8] and optical activity measurements [9–21]. The existence of quantum beating is due to the oscillation between left- and right-handed states, this being a typical example of a cyclic evolution.

It is well known that, in quantum mechanics, the initial and final state vectors of a cyclic evolution are related by a phase factor which can have observable consequences. Thus, Berry showed [22] that when the Hamiltonian is a function of a set of parameters and undergoes an adiabatic evolution along a closed curve in the parameter space, then a state that remains an eigenstate develops a geometrical

phase which depends only on that curve. Some years later, Aharonov and Anandan generalized this result defining a new geometric phase factor (which is a gauge invariant generalization of the phase factor found by Berry in the special case of adiabatic evolution) for any cyclic evolution of a quantum system [23]. Geometrical phases have been measured in many different fields of Physics [24]. For instance, in the field of high-energy physics, the geometric phase due to neutrino mixing has been studied in the context of the standard formulation of neutrino oscillations [25–27]. In molecular physics, geometric phases have been mainly studied in the context of conical intersections [28], where the Born–Oppenheimer approximation breaks down [24,29–31].

In this work, a different application of geometric phase effects in molecular physics is carried out. The goal is to look for alternative manifestations of PVED in chiral molecules [32]. The cyclic oscillation describing the stereomutation dynamics of chiral molecules gives place to geometric phases. These geometric phases are also explored for superposition states by using a canonical formulation in the description of the dynamics of chiral molecules [33]. In addition, following the model developed in [17], external chiral fields (circularly polarized electric fields) are shown to influence in the geometric phase. Furthermore, the interference pattern displayed by a superposition of chiral states in presence of external fields exhibits PVED-locking when the field amplitude equals the PVED in absolute value. This locking is also exhibited by the geometric phase.

2. Geometric phase for non-interacting chiral states

The isolated chiral molecule is modeled in a phenomenological way by a two-well potential within the Born–Oppenheimer approximation. The chiral states, $|L\rangle$ and $|R\rangle$, have the same energy E_0 . These states are connected to each other by tunneling through

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the double well barrier, so that if H is the Hamiltonian of the molecule, and following a common criteria for signs, then $\langle L|H|R\rangle = -\delta$, with $\delta > 0$. When a slight asymmetry in the double well potential is included due to the electroweak parity violation, the PVED is defined as $2\epsilon = \langle L|H|L\rangle - \langle R|H|R\rangle$. Taking $E_0 = 0$ as the origin of energies, the Hamiltonian describing the molecule is

$$\hat{H} = \delta\hat{\sigma}_x + \epsilon\hat{\sigma}_z, \quad (1)$$

where $\hat{\sigma}_{x,z}$ are the Pauli matrices ($\hbar = 1$).

The chiral states can be described in terms of the eigenstates by means of a rotation,

$$\begin{bmatrix} |L\rangle \\ |R\rangle \end{bmatrix} = \begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix} \begin{bmatrix} |1\rangle \\ |2\rangle \end{bmatrix}, \quad (2)$$

where the mixing angle, θ , is given by $\tan 2\theta = \delta/\epsilon$. From the time-dependent Schrödinger equation, $i\partial_t\Psi = H\Psi$, the time dependence of the $|L\rangle$ chiral state can be expressed as

$$|L\rangle(t) = e^{-iE_1 t}[\cos\theta|1\rangle - \sin\theta e^{-i(E_2-E_1)t}|2\rangle], \quad (3)$$

where $E_{1,2} = \pm\sqrt{\delta^2 + \epsilon^2} = \Delta$ are the eigenenergies of the system. After a period $T = 2\pi(E_1 - E_2)^{-1} = \pi\Delta^{-1}$, the chiral state acquires a phase according to

$$|L(T)\rangle = e^{i\phi_d}|L(0)\rangle \quad (4)$$

where

$$\phi_d = -2\pi \frac{E_1}{E_1 - E_2} = -\pi \quad (5)$$

is the so-called dynamical phase. Following [23], the total phase acquired by $|L\rangle$ during a single oscillation is

$$\phi = \phi_d + \int_0^T \left\langle L \left| i \frac{d}{dt} \right| L \right\rangle dt = \phi_d + \phi_g, \quad (6)$$

where ϕ_g is the geometric phase. This phase for the two chiral states are given by

$$\phi_g(L) = -\pi \cos 2\theta = -\pi \frac{\epsilon}{\sqrt{\delta^2 + \epsilon^2}}. \quad (7)$$

and

$$\phi_g(R) = \pi \cos 2\theta = -\phi_g(L). \quad (8)$$

Thus, chiral states only acquire a geometric phase *iff* parity is non-conserved. When tunneling matrix elements between chiral states are larger than the PVED between them, only dynamical phases survive. On the other hand, when tunneling is prevented due to a high barrier, the splitting between chiral states is only due to the PVED and an eventual measurement of the geometric phase should constitute an unequivocal manifestation of parity violation. For instance, CHBrClF or even alanine (both with practically infinite stereomutation time [1]) could be good candidates for such experimental measurements.

3. Geometric phase for non-interacting superposition states

Let us calculate the geometric phase for a superposition state of the form

$$|\Psi(t)\rangle = a_L(t)|L\rangle + a_R(t)|R\rangle, \quad (9)$$

where the complex amplitudes $a_{L,R}(t)$ are the solutions of the time dependent Schrödinger equation

$$\begin{bmatrix} \dot{a}_L(t) \\ \dot{a}_R(t) \end{bmatrix} = \begin{pmatrix} \epsilon & \delta \\ \delta & -\epsilon \end{pmatrix} \begin{bmatrix} a_L(t) \\ a_R(t) \end{bmatrix}. \quad (10)$$

The solutions of this system of linear equations are easily obtained by means of Laplace transforms

$$\begin{aligned} a_L(t) &= a_L^0 \cos \Delta t - \frac{i}{\Delta} (a_L^0 \epsilon + a_R^0 \delta) \sin \Delta t \\ a_R(t) &= \frac{1}{\delta} [(a_L^0 \epsilon + a_R^0 \delta) - \epsilon a_L^0] \cos \Delta t \\ &\quad + \frac{i}{\delta} \left[\frac{\epsilon}{\Delta} (a_L^0 \epsilon + a_R^0 \delta) - \Delta a_L^0 \right] \sin \Delta t, \end{aligned} \quad (11)$$

where $a_{L,R}^0 \equiv a_{L,R}(t=0)$. Inserting now these expressions in Eq. (6), the geometric phase can be written as

$$\phi_g(\Psi) = \pi \frac{\epsilon}{\Delta} (|a_{L,R}^0|^2 - |a_L^0|^2) - \pi \frac{\delta}{\Delta} (a_R^{0*} a_L^0 + a_L^{0*} a_R^0), \quad (12)$$

where $*$ denotes complex conjugate.

An alternative and very appealing way to re-express the geometrical phase given by (12) is by means of a recent canonical formulation of the dynamics of any isolated two-state system [33]. If the complex amplitudes are written in polar form as $a_{L,R}(t) = |a_{L,R}(t)|e^{i\Phi_{L,R}(t)}$ and the optical activity is defined as

$$z(t) \equiv |a_R(t)|^2 - |a_L(t)|^2 \quad (13)$$

and the phase difference between chiral states as

$$\Phi(t) \equiv \Phi_R(t) - \Phi_L(t), \quad (14)$$

then Eq. (12) can be expressed as

$$\phi_g(\Psi) = \pi \frac{\delta}{\Delta} \left(-\sqrt{1 - z_0^2} \cos \Phi_0 + \frac{\epsilon}{\delta} z_0 \right). \quad (15)$$

Recently, we have showed [33] that any isolated two-level system can be represented by the Hamiltonian

$$H = -\sqrt{1 - z^2(t)} \cos \Phi(t) + \frac{\epsilon}{\delta} z(t), \quad (16)$$

where $z(t)$ and $\Phi(t)$ can be seen as a pair of canonically conjugate variables obeying the Heisenberg equations of motion. These equations are formally identical to the Hamilton equations of motion,

$$\begin{aligned} \dot{z} &= -\frac{\partial H}{\partial \Phi} \\ \dot{\Phi} &= \frac{\partial H}{\partial z}, \end{aligned} \quad (17)$$

with $H = \langle \hat{H} \rangle_\Psi$. Now from Eqs. (13), (14) and (17), using a dimensionless time $t \rightarrow 2\delta t$, the equations of motion are explicitly written as

$$\begin{aligned} \dot{z}(t) &\equiv \frac{dz}{dt} = -\sqrt{1 - z^2} \sin \Phi \\ \dot{\Phi}(t) &\equiv \frac{d\Phi}{dt} = \frac{z}{\sqrt{1 - z^2}} \cos \Phi + \frac{\epsilon}{\delta}, \end{aligned} \quad (18)$$

leading to Harris and Stodolsky's seminar results on the appearance of quantum beats in parity violating chiral molecules [9].

Thus, in terms of these two new conjugate variables, the geometric phase for the superposition state here considered (Eq. (9)) turns out to be

$$\phi_g(\Psi) = \pi \frac{\delta}{\Delta} H_0, \quad (19)$$

where $H_0 \equiv H[z(t=0), \Phi(t=0)]$ is a conserved magnitude. This result is also obtained from the definition of the geometrical phase, Eq. (6). In what follows H instead of H_0 will be used.

Let us suppose now that the amplitudes are real ($\Phi_0 = 0$). In this case,

$$\phi_g(\Psi)/\pi = \frac{1}{\sqrt{1 + r^2}} + \left(rz_0 - \sqrt{1 - z_0^2} \right), \quad (20)$$

where $r \equiv \epsilon/\delta$ denotes the ratio between the two fundamental properties characterizing the chiral states. Notice that each chiral

molecule is represented by a particular value of such a ratio. This ratio is also directly linked to the mixing angle of rotation θ . Three limiting cases are worth mentioning for $\phi_g(r)$ which depends only on the initial population difference z_0

$$\begin{aligned}\lim_{r \rightarrow \infty} \phi_g(\Psi) &\rightarrow \pi z_0 \\ \lim_{r \rightarrow 0} \phi_g(\Psi) &\rightarrow -\pi \sqrt{1 - z_0^2} \\ \lim_{r \rightarrow 1} \phi_g(\Psi) &\rightarrow \frac{\pi}{\sqrt{2}} \left(z_0 - \sqrt{1 - z_0^2} \right).\end{aligned}\quad (21)$$

In Figure (1), the geometric phase is plotted versus z_0 for such limiting cases. As can be seen, this intrinsic property can be used to clearly discriminate between parity-conserving and parity-violating chiral molecules. In particular, the linear behavior ($r \rightarrow \infty$) could be found, for instance, for CHBrClF ($2\epsilon \approx 10^{-16}$ eV, and $\delta \ll 2\epsilon$) or alanine ($2\epsilon \approx 10^{-18}$ eV, and $\delta \ll 2\epsilon$). The parabolic behaviors could be displayed by T_2S_2 (short-dotted line; $2\epsilon \approx \delta \approx 10^{-16}$ eV and $r \rightarrow 1$) and H_2O_2 (long-dotted line; $2\epsilon \approx 10^{-18}$ eV, $\delta \approx 10^{-3}$ eV and $r \rightarrow 0$). For a complete table containing PVEDs and tunneling matrix elements for different chiral molecules, see [1] and references therein.

So far we have described how to distinguish between parity-odd and parity-even chiral molecules by looking at their geometric phase in terms of the population difference, $z(t)$, assuming $\Phi(0) = 0$. One can relax this constraint taking into account the opposite situation: $z(0) = 0$ (equal population for left and right chiral states) and assuming a non-zero initial phase, $\Phi(0)$. In this case, the geometric phase turns out to be

$$\phi_g(\Psi) = -\pi \frac{\delta}{\Delta} \cos \Phi_0. \quad (22)$$

In Figure (2) the dependence of the geometric phase with the initial phase is very sensitive to the ratio ϵ/δ . Each value of r represents a different chiral molecule. For chiral molecules where $\epsilon \lesssim \delta$, a cosine dependence is found. On the contrary, when $\epsilon \gg \delta$, the acquired geometric phase is zero.

On the other hand, information on interference experiments can be easily extracted from the probability density. As expected, the interference signal is of cosine-type according with

$$I \propto |\Psi(t)|^2 \propto 1 + 2|a_L(t)||a_R(t)| \cos \Phi(t) \quad (23)$$

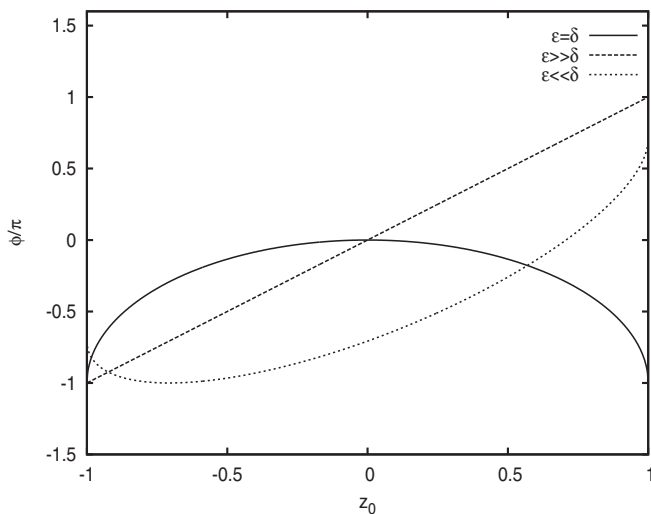


Figure 1. Geometric phase acquired by the superposition state of Eq. (9) during a single cyclic oscillation in terms of the initial population difference z_0 for different values of $r \equiv \epsilon/\delta$. Real initial amplitudes have been considered.

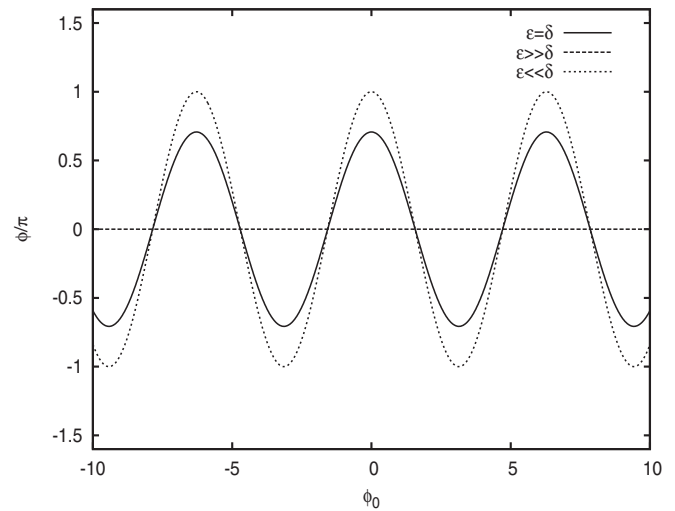


Figure 2. Geometric phase acquired by the superposition state of Eq. (9) during a single cyclic oscillation in terms of the initial phase of the chiral states, $\Phi(0)$, for different values of $r \equiv \epsilon/\delta$ and with $z(0) = 0$.

and one should be able to obtain information on $\cos \Phi(t)$, or simply the phase difference $\Phi(t)$, from this signal. It is interesting to note that Eq. (23) can be re-written as

$$I \propto 1 + \sqrt{1 - z^2(t)} \cos \Phi(t) = 1 + \frac{\epsilon}{\delta} z(t) - H. \quad (24)$$

From Eq. (24) we conclude that the interference signal between chiral states is time dependent only when $z_0 \neq 0$ and $\epsilon \neq 0$, otherwise it remains constant. Moreover, from Eq. (18) and taking $\Phi_0 = 0$ one obtains

$$z(t) = z_0 \left(\frac{r^2}{r^2 + 1} + \frac{1}{r^2 + 1} \cos 2\delta t \sqrt{1 + r^2} \right). \quad (25)$$

Thus, the time-dependence of the interference signal is

$$\begin{aligned}I &\propto 1 + \sqrt{1 - z^2(t)} \\ &= 1 - z_0 \left(\frac{r^2}{r^2 + 1} + \frac{1}{r^2 + 1} \cos 2\delta t \sqrt{1 + r^2} \right).\end{aligned}\quad (26)$$

We point out that this type of experiments could be used to look for signals of parity violation in chiral molecules.

Finally, it is also illustrative to study the effect produced by an external chiral perturbation, H' , in both the geometric phase and the interference signal shown in Eqs. (20) and (24). Following Ref. [17], consider a static (or time-averaged) external chiral influence. The Hamiltonian which extends trivially Eq. (1) is given by $\hat{H} = \delta \hat{\sigma}_x + \tilde{\epsilon} \hat{\sigma}_z$, where $\tilde{\epsilon} = \epsilon + \epsilon'$ and $\epsilon' = \langle L|H'|L \rangle = -\langle R|H'|R \rangle$. Under this approach, the new fundamental ratio changes from $r = \epsilon/\delta$ to $\tilde{r} = \tilde{\epsilon}/\delta$. Assuming a circularly polarized red laser as the external source of chirality, the energy difference between enantiomers due to H' turns out to be $\epsilon' \approx \pm 3 \cdot 10^{-24} E^2$ eV, where E is the intensity of the electric field [17,34]. Thus, an external field such that $200 < E < 2000$ Vm $^{-1}$ compensates a PVED between 10^{-16} and 10^{-18} eV [17]. As a consequence, the ratio $\tilde{r} = \tilde{\epsilon}/\delta$ becomes highly tunable by controlling the electric field.

In presence of the external field, the geometric phase of Eq. (20) is modified by the substitution $r \rightarrow \tilde{r}$ or $\epsilon \rightarrow \tilde{\epsilon}$,

$$\phi_g(\Psi)/\pi = \frac{1}{\sqrt{1 + \tilde{r}^2}} + \left(\tilde{r} z_0 - \sqrt{1 - z_0^2} \right). \quad (27)$$

In Figure (3) it is showed the geometric phase acquired by $|\Psi\rangle$ during a single cycle for different values of \tilde{r} , depending on the initial

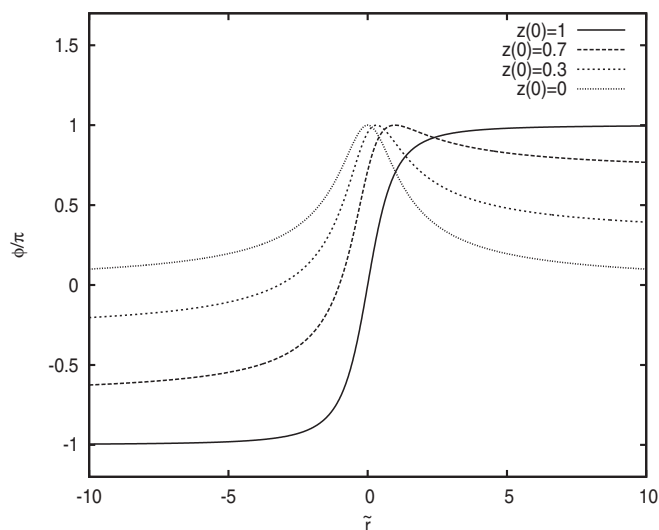


Figure 3. Geometric phase acquired by the superposition state of Eq. (9) during a single cyclic oscillation in terms of the ratio $\tilde{r} \equiv \tilde{\epsilon}/\delta$ for different initial populations, z_0 . We have taken real initial amplitudes.

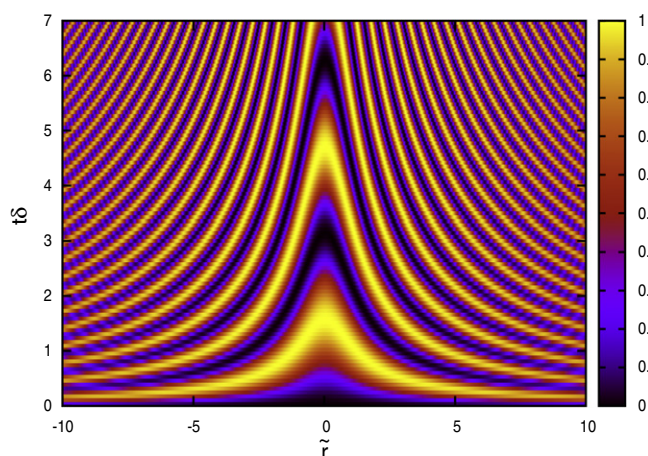


Figure 4. Interference between superposition states of Eq. (9) in terms of $t\delta$ and the ratio $\tilde{r} \equiv \tilde{\epsilon}/\delta$. We have taken real initial amplitudes.

population difference. Three limiting cases, depending whether $\tilde{r} \rightarrow -\infty$ (region one), $\tilde{r} \rightarrow 0$ (region two) or $\tilde{r} \rightarrow \infty$ (region three) are again considered. Notice that the signal of parity violation appears in region two since, in this region, the applied electric field can in principle be chosen such that $\epsilon' = -\epsilon$, $\tilde{r} = 0$ (PVED-locking). Thus, the rule of thumb is that the PVED detection can be carried out by annihilating its effect through an external field. To see how this locking could be used to detect the PVED, let us focus on two different molecules: CHBrClF and H₂O₂. In the first case, since parity violation is supposed to dominate the dynamics of stereomutation, the geometric phase behavior near $\tilde{r} = 0$ can be reached by controlling the external field up to lock the exact value of E such that $\tilde{r} = 0$. On the contrary, for H₂O₂, region two can only be mapped when $E = 0$.

The effect of this external field on the interference pattern given by Eq. (24) is such that

$$I \propto 1 + \frac{\tilde{\epsilon}}{\delta} z(t) - \tilde{H}, \quad (28)$$

where $\tilde{H} = H(\epsilon \rightarrow \tilde{\epsilon})$. Thus, Eq. (26) is now replaced by

$$I \propto 1 - z_0 \left(\frac{\tilde{r}^2}{\tilde{r}^2 + 1} + \frac{1}{\tilde{r}^2 + 1} \cos 2\delta t \sqrt{1 + \tilde{r}^2} \right), \quad (29)$$

which reflects the control on the oscillations between chiral states (the control of the electroweak optical activity [17]).

In Figure (4) the interference pattern obtained varying \tilde{r} through the control of the external field and at different times given by $t\delta$ is displayed. The periodicity in the perpendicular is due to the quantum beating of the optical activity. In this figure the region around $\tilde{r} \rightarrow 0$ shows the critical behavior of the interference pattern (the color key refers to the values of the intensity). Thus, the PVED-locking by means of a circularly polarized electric field gives place to periodic minima in the interference signal.

4. Conclusions

In this work we have studied the geometric phase acquired in the cyclic evolution of a chiral molecule, both in a pure chiral state and in a superposition of two chiral states. A simple two-state model that incorporates tunneling and parity violation effects into the dynamics of chiral molecules is able to describe the strong dependence of this geometric phase on the ratio between them. A canonical formulation of the oscillation dynamics of chiral molecules to calculate the geometric phase in terms of two measurable canonically conjugate variables (the population and phase difference between chiral states) has been used. It has been shown that an eventual detection of this geometric phase constitutes a way of proving the existence of the PVED, showing how this could be achieved using chiral fields by PVED-locking (in particular circularly polarized electric fields). This locking would give place to a clear signature of parity violation in the interference pattern between chiral states. This study can be extended to include mean-field effects in the geometric phase. Work in this direction is now in progress.

Acknowledgement

This work has been funded by the MICINN (Spain) through Grant Nos. CTQ2008-02578, FIS2007-62006, FIS2010-18132, and the Juan de la CIERVA program (P.B.).

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