Dissipative geometric phase and decoherence in parity-violating chiral molecules

A. Dorta-Urra, H. C. Peñate-Rodríguez, P. Bargueño, G. Rojas-Lorenzo, and S. Miret-Artés

Citation: J. Chem. Phys. **136**, 174505 (2012); doi: 10.1063/1.4707735
View online: http://dx.doi.org/10.1063/1.4707735
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v136/i17
Published by the American Institute of Physics.

Dissipative geometric phase and decoherence in parity-violating chiral molecules

A. Dorta-Urra,[1] H. C. Peñate-Rodríguez,[2,3] P. Bargueño,[4,a)] G. Rojas-Lorenzo,[2,3] and S. Miret-Artés[3]
[1]*Unidad asociada UAM-CSIC, Instituto de Física Fundamental (CSIC), Serrano 123, E-28006 Madrid, Spain*
[2]*Instituto Superior de Tecnología y Ciencias Aplicadas, Ave. Salvador Allende y Luaces, Quinta de Los Molinos, Plaza, La Habana 10600, Cuba*
[3]*Instituto de Física Fundamental (CSIC), Serrano 123, E-28006 Madrid, Spain*
[4]*Departamento de Física de Materiales, Universidad Complutense de Madrid, E-28040 Madrid, Spain*

(Received 18 January 2012; accepted 12 April 2012; published online 3 May 2012)

Within a generalized Langevin framework for open quantum systems, the cyclic evolution of a two-level system is analyzed in terms of the geometric phase extended to dissipative systems for Ohmic friction. This proposal is applied to the dynamics of chiral molecules where the tunneling and parity violating effects are competing. The effect of different system-bath coupling functions in the dissipated energy is shown to be crucial to understand the behavior of the geometric phase as well as the decoherence displayed by the corresponding interference patterns. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4707735]

I. INTRODUCTION

Nowadays measuring the energy difference between enantiomers of chiral molecules is considered as one of the most challenging experiments.[1] After more than 40 years of research, the parity-violating energy difference (PVED) between the two enantiomers of chiral molecules (a consequence of the theory of electroweak interactions), still remains elusive for an experimental detection. This PVED is estimated to be between 10^{-13} and 10^{-21} eV (for recent reviews see Refs. 2–7) but no conclusive energy difference has been reported up to date.[8–10] Due to the weakness of the effect, extremely precise theoretical calculations are needed to propose appropriate molecular candidates to guide the experiment.[11–14] Since the first experimental suggestion,[15] several techniques have been proposed for the observation of parity violation in molecular systems such as, for example, laser spectroscopy on vibrational transitions,[8,10,14,16] electronic,[17,18] Mossbauer[9,19] and NMR spectroscopies,[20,21] and optical activity measurements.[22–35] In the last type of measurements, time dependent optical activity is proposed in chiral molecules creating superpositions of eigenstates of the two asymmetric wells, where the tunneling and PVED contributions are of the same order of magnitude.[22,27] Thus, such experiments would provide indirect information on the PVED by comparison with the tunneling splittings (for an exhaustive list of tunneling splittings and PVEDs, see Table 6 of Ref. 7 and references therein).

Essentially, the quantum beating of the optical activity is a consequence of the oscillation between left- and right-handed states, this being a typical example of a cyclic evolution. A well known consequence of quantum mechanics is that the initial and final state vectors of a cyclic evolution are related by a phase factor with observable consequences, two paradigmatic examples being the Berry[36] and Aharonov-Anandan phases.[37] Although geometrical phases have been measured in many different fields of physics,[38] in molecular physics they have been mainly studied in the context of conical intersections,[39] where the Born-Oppenheimer approximation breaks down[38,40–42] (for a recent study on geometric phases in polyatomic molecules from a gauge field theory perspective, see Ref. 43). In a recent work,[44] we have looked for alternative manifestations of the PVED in isolated chiral molecules (described as a pure state) by analyzing the geometric phase as a consequence of the stereomutation dynamics of these molecules. In particular, we have derived the explicit dependence of the geometric phase on the essential parameters describing this stereomutation process. Even more, the geometric phase has also been explored for superposition states by using a canonical formulation in the description of the corresponding dynamics[45] by means of a Caldeira-Legget-like Hamiltonian.[46] External chiral fields (circularly polarized electric fields) have been shown to influence the geometric phase. Furthermore, the interference pattern displayed by such a superposition of states in the presence of external fields exhibits PVED-locking when the amplitude of the field equals the PVED in absolute value. This locking is also exhibited by the geometric phase.

There are several extensions of the geometric phase concept to open quantum systems based on quantum trajectories issued from the stochastic Schrödinger equation,[47,48] quantum interferometry,[49–53] and the kinematic approach.[54,55] However, as far as we know, there is no definition of the geometric phase in the Langevin framework which is equivalent to the usual density matrix approach.[46] In this work, a simple definition for the geometric phase acquired by chiral states in the corresponding cyclic evolution when interactions with the environment are taken into account is proposed and analyzed.

a)p.bargueno@fis.ucm.es.

In particular, the consequences of the competition between tunneling and parity violation when an Ohmic friction is assumed in an eventual measurement of the geometric phase and the decoherence displayed by interference patterns in this chiral dynamics are studied.

II. THEORY

A. General considerations

Let us remember that an isolated chiral molecule can be modelled in a phenomenological way by a two-well potential within the Born-Oppenheimer approximation. We consider that the chiral states, $|L\rangle$ and $|R\rangle$, have the same energy E_0. These states are connected to each other by tunneling through the double well barrier. If $\hat{H}$ is the Hamiltonian of the molecule then $\langle L|\hat{H}|R\rangle = -\delta$, with $\delta > 0$, following a common criteria for signs. When a slight asymmetry in the double well potential is included due to the electroweak parity violation, the PVED is defined as $2\epsilon = \langle L|\hat{H}|L\rangle - \langle R|\hat{H}|R\rangle$. Taking $E_0 = 0$ as the origin of energies, the Hamiltonian describing the molecule is

$$\hat{H} = \delta\hat{\sigma}_x + \epsilon\hat{\sigma}_z, \tag{1}$$

where $\hat{\sigma}_{x,z}$ are the Pauli matrices (and $\hbar = 1$). The chiral states can be described in terms of the eigenstates by means of a rotational angle θ given by $\tan 2\theta = \delta/\epsilon$.

Following Aharonov and Anandan,[37] the geometric phase acquired by the pure state $|L\rangle$ during a single oscillation of period T in a cyclic evolution is

$$\phi_g(L) = \pi + \int_0^T \langle L|i\frac{d}{dt}|L\rangle dt = \pi + \int_0^T \langle\hat{H}\rangle_{|L\rangle}, \tag{2}$$

which turns out to be[44]

$$\begin{aligned}\phi_g(L) &= -\phi_g(R)\\ &= \pi(1-\cos 2\theta) = \pi\left(1 - \frac{\epsilon}{\sqrt{\delta^2+\epsilon^2}}\right),\end{aligned} \tag{3}$$

and where the second term is known as the dynamical phase. Thus, chiral states only acquire a geometric phase due to stereomutation *iff* parity is non-conserved. 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 be strictly zero. Let us note that, as interactions with the environment lead to tunnel suppression (see, for example, the dissipative-induced racemization shown in Ref. 45), a strong dependence of the geometric phase on the PVED is expected when considering either long times or strong dissipation, irrespective of the height of the barrier.

B. Generalized Langevin dynamics of chiral molecules

An alternative and very appealing way to express the geometrical phase of a linear combination of chiral states is by means of a canonical formulation.[44,45] Let us consider a state of the form

$$|\Psi(t)\rangle = a_L(t)|L\rangle + a_R(t)|R\rangle. \tag{4}$$

Then, if the corresponding complex amplitudes are written in polar form as $a_{L,R}(t) = |a_{L,R}(t)|e^{i\Phi_{L,R}(t)}$, the optical activity is defined as $z(t) \equiv |a_R(t)|^2 - |a_L(t)|^2$, and the phase difference between chiral states as $\Phi(t) \equiv \Phi_R(t) - \Phi_L(t)$, then the geometric phase for this superposition of chiral states is given by

$$\phi_g(\Psi) = \pi + \pi\frac{\delta}{\Delta}\left(-\sqrt{1-z_0^2}\cos\Phi_0 + \frac{\epsilon}{\delta}z_0\right), \tag{5}$$

where $z_0 = z(t=0)$, $\Phi_0 = \Phi(t=0)$, and $\Delta = \sqrt{\delta^2+\epsilon^2}$.

Any isolated two-level system has been showed to be described by the Hamiltonian[45]

$$H = -\sqrt{1-z^2}\cos\Phi + \frac{\epsilon}{\delta}z, \tag{6}$$

where z and Φ can be seen as a pair of canonically conjugate variables. In the quantum domain, these variables obey the Heisenberg equations of motion which are formally identical to the Hamilton equations of motion, $\dot{z} = -\partial H/\partial\Phi$ and $\dot{\Phi} = \partial H/\partial z$. Thus, in terms of these two new conjugate variables, the geometric phase given by Eq. (5) turns out to be[44]

$$\phi_g(\Psi) = \pi\left(1 + \frac{\delta}{\Delta}H_0\right), \tag{7}$$

where $\langle\hat{H}\rangle_\Psi = H_0 \equiv H[z(t=0), \Phi(t=0)]$ denotes the average value of the molecular energy which is a conserved magnitude when dealing with a closed system. It should be noticed that the first term of the Hamiltonian (6) accounts for the tunneling process and the second one for the underlying PVED asymmetry.

Noting that Φ and z play the role of a generalized coordinate and momentum, respectively, one can introduce interactions with the environment by means of a system-bath bilinear coupling via a Caldeira-Legget-like Hamiltonian expressed as[44]

$$\begin{aligned}H = &-\sqrt{1-z^2}\cos\Phi + \frac{\epsilon}{\delta}z\\ &+\frac{1}{2}\sum_i\left(\Lambda_i z_i^2 + \frac{\Phi_i^2\omega_i^2}{\Lambda_i}\right)\\ &-\Phi\sum_i c_i\Phi_i + \Phi^2\sum_i c_i^2\Lambda_i,\end{aligned} \tag{8}$$

where the sums run over the coordinates of the bath oscillators $\{z_i, \Phi_i\}$ and Λ_i, c_i, and ω_i are suitable dimensionless constants representing generalized masses, couplings with the environment, and oscillator frequencies, respectively. Without loss of generality, notice that these bath variables could also be alternatively written in terms of the usual harmonic oscillator ones (positions and momenta). In any case, these environmental degrees of freedom can be exactly eliminated from the equations of motion. On the other hand, when dealing with phases or angles, the bilinear coupling could be questionable due to the fact that the corresponding Hamiltonian does not display the periodicity of the problem at hand. For example,

in the rotational tunneling process (see Ref. 56 and references therein) the environmental coupling has the same periodicity as the hindering potential. In our canonical formalism for chiral molecules, the generalized position is a phase variable and the molecule-bath coupling should be periodic in Φ. Thus, we could consider the following generalized Hamiltonian:

$$H = -\sqrt{1-z^2}\cos\Phi + \frac{\epsilon}{\delta}z + \frac{1}{2}\sum_i\left(\Lambda_i z_i^2 + \frac{\Phi_i^2\omega_i^2}{\Lambda_i}\right) - f(\Phi)\sum_i c_i\Phi_i + f^2(\Phi)\sum_i c_i^2\Lambda_i, \tag{9}$$

where the periodicity of the coupling is given by the specific choice of the function $f(\Phi)$. The corresponding coupled generalized Langevin equations are then given by (dimensionless time units are used, $t \to 2\delta t$)

$$\dot{z} = -\sqrt{1-z^2}\sin\Phi - \frac{df(\Phi)}{d\Phi}\int_0^t \gamma(t-t')\frac{df(\Phi)}{d\Phi}\dot{\Phi}(t')\,dt' + \frac{df(\Phi)}{d\Phi}\xi(t),$$
$$\dot{\Phi} = \frac{z}{\sqrt{1-z^2}}\cos\Phi + \frac{\epsilon}{\delta}, \tag{10}$$

where

$$\gamma(t) = \sum_i \Lambda_i c_i^2\cos\omega_i(t-t') \tag{11}$$

is the damping kernel and

$$\xi(t) = \textstyle\sum_i\, c_i\Lambda_i\,(\Phi_i(0)\cos\omega_i t + z_i(0)\sin\omega_i t) - c_i^2\Lambda_i\Phi_0 f(\Phi_0)\frac{df(\Phi)}{d\Phi}\cos\omega_i t \tag{12}$$

represents a stochastic force, depending on the initial conditions of both the system and the bath. The temperature will be considered high enough in order to neglect contributions coming from the zero point motions of bath oscillators. Thus, when averaging over the bath variables, this force vanishes leading to a pure dissipative dynamics in terms of the average quantities of the system which will be again denoted (for simplicity) by z and Φ. In other words, Eqs. (10) will be solved numerically for the average quantities and where the average stochastic force is zero. We point out that when reaching cold temperatures, it would be necessary to consider only the two lowest states thermally populated and the noise should be treated quantum mechanically.

If only dissipative dynamics is considered, Eqs. (10) for the average quantities, z and Φ, can be derived from the following effective Hamiltonian:

$$H_\gamma(t) = -\sqrt{1-z^2}\cos\Phi + \frac{\epsilon}{\delta}z + \gamma\dot{\Phi}\int_0^\Phi\left(\frac{df(\Phi')}{d\Phi'}\right)^2 d\Phi', \tag{13}$$

which explicitly depends on friction and the generalized velocity, $\dot{\Phi}$. Let us point out that H_γ actually represents the non-conserved energy of the chiral system in the presence of dissipation due to the coupling with the bath.

At this point, a quite natural and straightforward extension of the geometric phase, displayed by a superposition of chiral states during a cycle of period T, can be proposed from Eq. (2) to the case of dissipative dynamics as follows:

$$\phi_g^\gamma(\Psi) \equiv \pi + \int_0^T H_\gamma(t)\,dt. \tag{14}$$

This quantity plays the same role as that used in the definition of geometric phase given by Eq. (2). After Eq. (14), it is easy to see that the non-dissipative phase is recovered taking $\gamma = 0$ and noting that $H_\gamma \to H_0$, which is a conserved magnitude (we would like to point out the formal similarities between the geometric phase given by our Eq. (14) and that of Ref. 55 (Eq. 21), derived from Lindblad's formalism). It should also be stressed here the importance of the dissipated energy in one period of the cyclic evolution for the evaluation of the geometric phase.

C. Role of the coupling function

Let us now analyze the effect of different generalized couplings in the dissipative dynamics. If Ohmic friction is assumed, the generalized Langevin equations given by Eqs. (10) are rewritten as

$$\dot{z} = -\sqrt{1-z^2}\sin\Phi - \gamma\left(\frac{df(\Phi)}{d\Phi}\right)^2\dot{\Phi},$$
$$\dot{\Phi} = \frac{z}{\sqrt{1-z^2}}\cos\Phi + \frac{\epsilon}{\delta}. \tag{15}$$

If the usual bilinear coupling is considered, the dissipated energy is given by

$$H_\gamma(t) = -\sqrt{1-z^2}\cos\Phi + \frac{\epsilon}{\delta}z + \gamma\Phi\dot{\Phi}. \tag{16}$$

On the other hand, when periodic coupling is assumed, the most standard functions to be considered are a sine or cosine function, $f^{(1)}(\Phi) = \sqrt{2}\sin\Phi$ and $f^{(2)}(\Phi) = \sqrt{2}\cos\Phi$. The following effective Hamiltonians are straightforwardly obtained to be

$$H_\gamma^{(1,2)}(t) = -\sqrt{1-z^2}\cos\Phi + \frac{\epsilon}{\delta}z + \gamma\dot{\Phi}\left(\Phi \pm \frac{\sin 2\Phi}{2}\right) \tag{17}$$

where the superscripts (1, 2) correspond to the plus and minus sign, respectively. For the cosine-type coupling, when the phase is a small quantity, the term involving the friction coefficient is very small or even zero for a certain period of time. This fact should lead to a lower decaying behavior with time. And, finally, depending on the initial conditions, the starting value of the decaying system energy will be different.

D. Decoherence of interference patterns

For this dissipative dynamics, information on interference experiments can be straightforwardly extracted from the probability density. The typical interference signal is of cosine-type according to

$$I \propto |\Psi(t)|^2 \propto 1 + 2|a_L(t)||a_R(t)|\cos\Phi(t) \tag{18}$$

and one should be able to obtain information of the phase from the cosine oscillations. Using the effective Hamiltonian approach here developed, the total intensity of the interference pattern for the Ohmic case is given now by

$$I \propto 1 + \frac{\epsilon}{\delta} z - H_\gamma = 1 + \sqrt{1 - z^2} \cos \Phi - \gamma \dot{\Phi} \int_0^\Phi \left(\frac{df(\Phi')}{d\Phi'} \right)^2 d\Phi, \quad (19)$$

where z, Φ are the solutions of Eqs. (15). This type of experiments could also be used to look for signals of parity violation in chiral molecules. Furthermore, the presence of dissipation in this effective Hamiltonian will lead to the suppression of quantum interference, that is, to decoherence. The quantum interference (coherence) is given by Eq. (19) when replacing H_γ by H_0.

III. RESULTS

It is very instructive to analyze first how the energy is dissipated with time for different coupling functions when the tunneling or the PVED asymmetry is competing. This magnitude has been previously shown to play a critical role in the evaluation of the geometric phase and the time evolution of interference patterns.

For the bilinear coupling, Fig. 1 shows the time dependence of H_γ for $\epsilon = 0$ (symmetric wells) and $\delta = 0.5$ at different values of the friction coefficient, γ (given in units of 2δ), and with initial conditions $z_0 = 0.999$ and $\Phi_0 = 0$. In this case, the tunneling process only rules the dynamics and H_γ displays a global exponential relaxation. With the correct dimensions, the expected asymptotic behavior is reproduced, that is, $H_\gamma \to -2\delta$ for long times. This asymptotic limit is due to the tunneling blocking which occurs with friction is acting at very long times. The linear term involved in Eq. (6) plays no role. Therefore, the system tends to an eigenstate of the isolated chiral molecule. Figure 1 also shows, for $\gamma = 0$, the conserved energy of the system. This behavior is expected to occur, for example, in molecules such as H_2O_2 or H_2S_2, which have a ratio of $\epsilon/\delta \simeq 10^{-15}$ and 10^{-6}, respectively.[7]

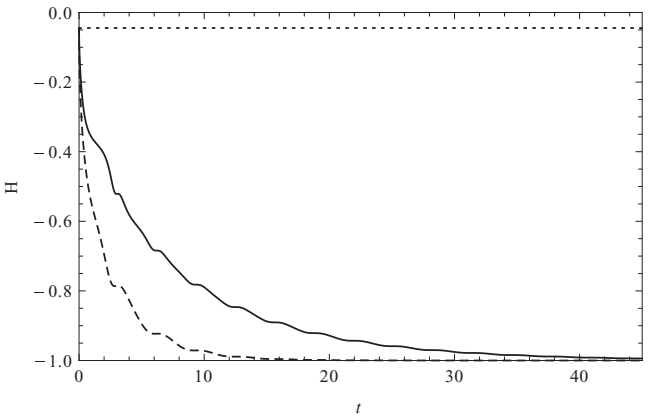

FIG. 1. Time dependence of H_γ for different values of the friction [$\gamma = 0$ (dotted), $\gamma = 0.1$ (solid), and $\gamma = 0.3$ (dashed)] when tunneling only rules the dynamics of stereomutation ($\epsilon = 0$, symmetric wells).

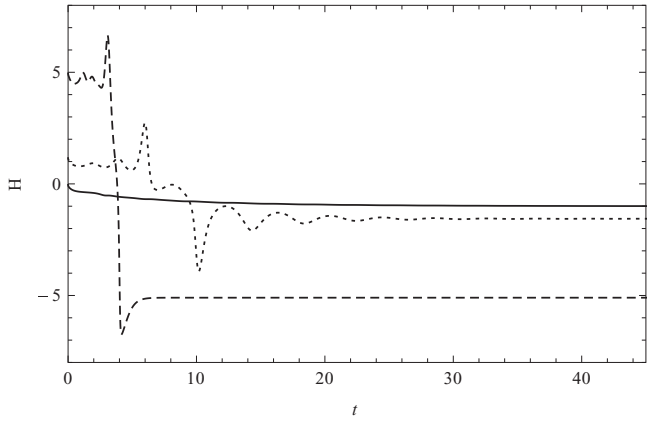

FIG. 2. Time dependence of H_γ for different values of the PVED [$\epsilon/\delta = 0$ (solid line), $\epsilon/\delta = 1.2$ (dotted line), and $\epsilon/\delta = 5$ (dashed line)]. We have taken $\gamma = 0.1$, $z_0 = 0.999$, and $\Phi_0 = 0$.

A drastic scenario takes place when the PVED is present, $\epsilon \neq 0$. As shown in Fig. 2, and for different ratios ϵ/δ, no global behavior is observed in the time evolution of the dissipated energy, $H_\gamma(t)$, except for the solid curve which displays the behavior with no PVED asymmetry. The other two values for the ratio $\epsilon/\delta = 1.2, 5$ correspond to two drastically different dynamics. The first value describes a dynamics where the tunneling and the PVED asymmetry are competing and, in the second value, the dynamics is without tunneling. At long times, in both cases, the system energy tends again to the eigenstate $-2\Delta = -2\sqrt{\delta^2 + \epsilon^2}$ following a different behavior. In the competing case, the oscillations displayed by the dissipative system are due to the presence of tunneling except to very long times where this process is inhibited due to the friction. On the contrary, in the second case, the asymptotic energy is reached after a short period of time but in an abrupt way since tunneling is not present and the linear term of Hamiltonian (6) dominates the dynamics. An inspection of Fig. 2 reveals that the most rich structure occurs for molecules such that $\epsilon/\delta \simeq 1$, as is the case of D_2Se_2.[7]

In Fig. 3, the comparison between the dissipative dynamics driven by bilinear, sine, and cosine coupling functions is

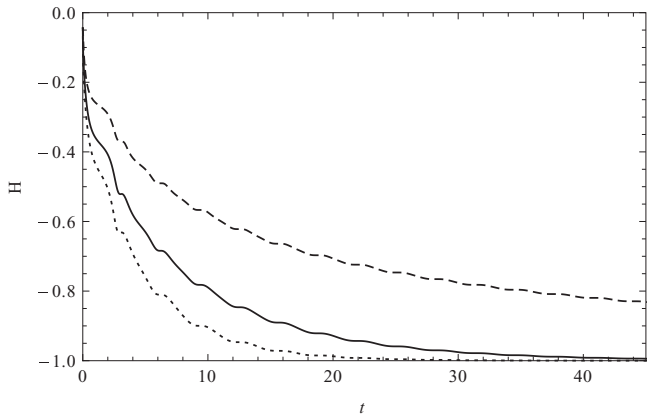

FIG. 3. Time dependence of H_γ for $\epsilon/\delta = 0$, $\gamma = 0.1$ and different couplings (bilinear, sine, and cosine dissipations depicted by solid, dotted, and dashed lines, respectively). We have taken $z_0 = 0.999$ and $\Phi_0 = 0$ for the initial conditions.

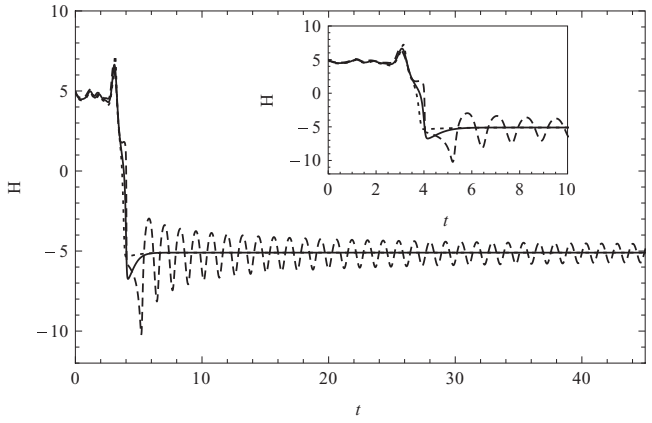

FIG. 4. Time dependence of H_γ for $\epsilon/\delta = 5$ and different couplings (solid, dotted, and dashed for bilinear, sine, and cosine coupling functions, respectively). We have taken $z_0 = 0.999$ and $\Phi_0 = 0$ as the initial conditions of the dynamics.

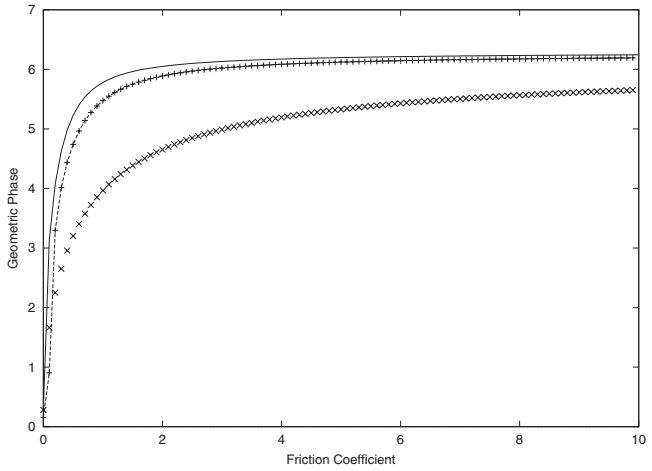

FIG. 5. Geometric phase in terms of the friction for different values of the PVED [$\epsilon = 0$ (solid line) and $\epsilon/\delta = 0.3$ (solid line with points)]. We have taken $z_0 = 0.999$ and $\Phi_0 = 0$ as the initial conditions of the chiral dynamics. The points (without line) represent the geometric phase for a cosine-type coupling and $\epsilon = 0$.

shown for the case of parity-conserving molecules (such as H_2O_2). The dissipative dynamics is shown to be not very different in case of bilinear and sine couplings, with the exception of small discrepancies shown regarding the decay time. On the contrary, when a cosine-type coupling is considered, dissipative effects are shown to be strongly reduced. As expected, the elapsed time needed to reach complete localization is enormously high in the case of cosine coupling.

As observed in Fig. 4, when the PVED asymmetry dominates mainly the chiral dynamics, $\epsilon/\delta = 5$, the main differences among the bilinear, sine-, and cosine-type coupling functions are clearly manifested at long times. Thus, when the dissipative dynamics is due to both bilinear and sine-type couplings, the energy tends very rapidly to the corresponding eigenstate. On the contrary, for cosine dissipation, the energy performs regular oscillations around the same asymptotic value, which will be reached for very, very long times.

Once the dissipated energy has been analyzed in terms of the different coupling functions, the next step is to show how the geometric phase depends on the friction coefficient. The explicit dependence of the dynamical phase (when the π-phase is neglected) on the friction coefficient γ is deduced from solving numerically Eqs. (15) and then using the previous definition given by Eq. (14). In Fig. 5, the geometric phase is displayed when $\epsilon = 0$ (solid line) and $\epsilon/\delta = 0.3$ (solid line with points) for the bilinear coupling. We note that $\phi_g^\gamma \to \pi(\delta/\Delta)H_0$ when $\gamma \to 0$ according to Eq. (7). On the contrary, with the friction, the geometric phase reaches a plateau given by $\phi_g(\gamma \to \infty) \to 2\pi$. This behavior is a direct consequence of tunneling suppression. Thus, one can speculate on using an appropriate tuning of the environment (by changing the pressure, the temperature, or the density of a surrounding gas, for example) to test the dependence of the geometric phase on the friction coefficient and on the PVED. Moreover, when a cosine-type coupling is considered (points in Fig. 5), noticeable differences can be shown between the geometric phase in the bilinear case and in the present situation. It should be emphasized that, when the PVED is present, the plateau displayed by the geometric phase is reached before (at slightly smaller friction coefficients) compared to the situation in which tunneling prevails.

Finally, Fig. 6 displays the time-dependent interference signal for different kinds of coupling for $\gamma = 0.1$ and when PVED dominates over the tunneling process. For comparison, we have also depicted the non-dissipative case (dashed-dotted line). When $\gamma = 0$, the interference signal displays regular cosine oscillations for all times (coherence). With Ohmic friction, in all cases, the coherence is destroyed (decoherence). If a bilinear coupling is assumed, strong oscillations are present at short times, although the final damping of the signal can be appreciated when $t > 5$. The main differences between sine (dotted line) and cosine dissipation (dashed line) appear at $t > 5$. In this region, damping leads to an interference signal which is quite similar to the one shown by the bilinear case. On the contrary, as expected, with cosine dissipation, damping gives place to an oscillating signal whose amplitude is again very slowly decreased. At short times, similar behaviors are displayed for different coupling functions.

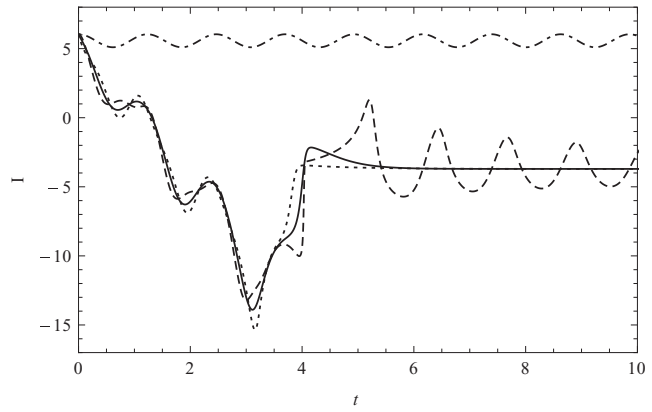

FIG. 6. Interference signal for $\epsilon/\delta = 5$ and bilinear (solid line), sine- (dotted line), and cosine-type couplings (dashed line). The non-dissipative signal is depicted with dashed-dotted lines. We have taken $\gamma = 0.1$, $z_0 = 0.999$, and $\Phi_0 = 0$.

IV. CONCLUSION

In this work, we have put in evidence the fundamental role played by the parity-violating energy difference in the dissipative stereomutation dynamics, within a canonical description of chiral molecules in the Langevin framework. The nonlinearity exhibited by the coupled equations describing this process competing with tunneling has shown to be very rich. The canonical formalism has allowed us to define an effective Hamiltonian for Ohmic friction for any dissipative two-level system interacting with a bath of harmonic oscillators via a generalized coupling. In particular, the effects of two different periodic (sine and cosine) coupling functions have been rationalized in terms of strong and weak dissipation, respectively. A straightforward extension of the definition of the geometric phase in pure states to open quantum systems with Ohmic friction has been proposed. Finally, the role of different dissipative effects in the energy, the geometric phase, and decoherence displayed by interference patterns of this cyclic evolution has been discussed.

ACKNOWLEDGMENTS

This work has been funded by the MICINN (Spain) through Grant Nos. CTQ2008-02578, FIS2010-18132, and by the Comunidad Autónoma de Madrid, Grant No. S-2009/MAT/1467. P.B. acknowledges a Juan de la Cierva fellowship from the MICINN and A.D.-U. acknowledges a JAE fellowship from CSIC. H.C.P.-R. and G.R.-L. acknowledge a scientific project from INSTEC.

[1] N. Jones, Nature (London) **481**, 14 (2012).
[2] R. Berger, "Relativistic electronic structure theory: Part 2. Applications," in *Parity-Violation Effects in Molecules*, edited by P. Schwerdtfeger (Elsevier, Netherlands, 2004).
[3] M. Quack, J. Stohner, and M. Willeke, Annu. Rev. Phys. Chem. **59**, 741 (2008).
[4] B. Darquié, C. Stoeffler, S. Zrig *et al.*, Chirality **22**, 870 (2010).
[5] P. Schwerdtfeger, "The search for parity violation in chiral molecules," in *Computational Spectroscopy* (Wiley-VCH, Weinheim, 2010).
[6] M. Quack, Faraday Discuss. **150**, 533 (2011).
[7] M. Quack, "Fundamental symmetries and symmetry violations from high-resolution spectroscopy," in *Handbook of High-resolution Spectroscopy*, edited by M. Quack and F. Merkt (Wiley-VCH, 2011).
[8] C. Daussy, T. Marrel, A. Amy-Klein *et al.*, Phys. Rev. Lett. **83**, 1554 (1999).
[9] A. S. Lahamer, S. M. Mahurin, R. N. Compton *et al.*, Phys. Rev. Lett. **85**, 4470 (2000).
[10] M. Ziskind *et al.*, Eur. J. Phys. D **20**, 219 (2002).
[11] J. K. Laerdahl, P. Schwerdtfeger, and H. M. Quiney, Phys. Rev. Lett. **84**, 3811 (2000).
[12] J. Thyssen, J. K. Laerdahl, and P. Schwerdtfeger, Phys. Rev. Lett. **85**, 3105 (2000).
[13] R. Bast and P. Schwerdtfeger, Phys. Rev. Lett. **91**, 023001 (2003).
[14] F. de Montigny, R. Bast, A. S. Pereira-Gomes *et al.*, Phys. Chem. Chem. Phys. **12**, 8792 (2010).
[15] V. S. Letokhov, Phys. Lett. A **53**, 275 (1975).
[16] M. Quack and J. Stohner, Phys. Rev. Lett. **84**, 3807 (2000).
[17] M. Quack, Chem. Phys. Lett. **132**, 147 (1986).
[18] R. Berger, Phys. Chem. Chem. Phys. **5**, 12 (2003).
[19] I. B. Khriplovich, Sov. Phys. JETP **52**, 177 (1980).
[20] A. L. Barra, J. B. Robert, and L. Wiesenfeld, Phys. Lett. A **115**, 443 (1986).
[21] NMR experiments currently underway in the group of R. N. Compton (Tennessee).
[22] R. A. Harris and L. Stodolsky, Phys. Lett. B **78**, 313 (1978).
[23] R. A. Harris and R. Silbey, J. Chem. Phys. **78**, 7330 (1983).
[24] R. A. Harris, Chem. Phys. Lett. **223**, 250 (1994).
[25] R. A. Harris, Y. Shi, and J. A. Cina, J. Chem. Phys. **101**, 3459 (1994).
[26] R. Silbey and R. A. Harris, J. Chem. Phys. **93**, 7062 (1989).
[27] J. Cina and R. A. Harris, J. Chem. Phys. **100**, 2531 (1994).
[28] R. A. Harris and L. Stodolsky, J. Chem. Phys. **74**, 2145 (1981).
[29] R. A. Harris, Chem. Phys. Lett. **365**, 343 (2002).
[30] A. J. MacDermott and R. A. Hegstrom, Chem. Phys. **305**, 55 (2004).
[31] P. Bargueño, I. Gonzalo, and R. Pérez de Tudela, Phys. Rev. A **80**, 012110 (2009).
[32] P. Bargueño, I. Gonzalo, R. Pérez de Tudela, and S. Miret-Artés, Chem. Phys. Lett. **483**, 204 (2009).
[33] I. Gonzalo, P. Bargueño, R. Pérez de Tudela, and S. Miret-Artés, Chem. Phys. Lett. **489**, 127 (2009).
[34] P. Bargueño, R. Pérez de Tudela, S. Miret-Artés, and I. Gonzalo, Phys. Chem. Chem. Phys. **13**, 806 (2011).
[35] P. Bargueño, S. Miret-Artés, and I. Gonzalo, Phys. Chem. Chem. Phys. **13**, 850 (2011).
[36] M. V. Berry, Proc. R. Soc. London, Ser. A **392**, 45 (1984).
[37] Y. Aharonov and J. Anandan, Phys. Rev. Lett. **58**, 1593 (1986).
[38] A. Bohm *et al.*, *The Geometric Phase in Quantum Systems: Foundations, Mathematical Concepts, and Applications in Molecular and Condensed Matter Physics* (Springer, 2003).
[39] G. A. Worth and L. S. Cederbaum, Ann. Rev. Phys. Chem. **55**, 127 (2004).
[40] C. A. Mead, Rev. Mod. Phys. **64**, 51 (1992).
[41] M. S. Child, Adv. Chem. Phys. **124**, 1 (2002).
[42] S. C. Althorpe, J. C. Juanes-Marcos, and E. Wrede, Adv. Chem. Phys. **138**, 1 (2008).
[43] C. Wittig, Phys. Chem. Chem. Phys. **14**, 6409 (2012).
[44] H. C. Peñate-Rodríguez *et al.*, Chem. Phys. Lett. **523**, 49 (2012).
[45] P. Bargueño *et al.*, Chem. Phys. Lett. **516**, 29 (2011).
[46] U. Weiss, *Quantum Dissipative Systems*, 2nd ed., Series in Modern Condensed Matter Physics, Vol. 10 (World Scientific, Singapore, 1999).
[47] A. Bassi and E. Ippoliti, Phys. Rev. A **73**, 062104 (2006).
[48] N. Burić and M. Radonjić, Phys. Rev. A **80**, 014101 (2009).
[49] E. Sjökvist, Phys. Rev. Lett. **85**, 2845 (2000).
[50] R. Bhandary, Phys. Rev. Lett. **89**, 268901 (2002).
[51] E. Sjökvist, Phys. Rev. A **70**, 052109 (2004).
[52] R. Bhandary, Phys. Rep. **281**, 1 (1997).
[53] J. Du *et al.*, Phys. Rev. Lett. **91**, 100403 (2003).
[54] N. Mukunda and R. Simon, Ann. Phys. **228**, 205 (1993).
[55] D. M. Tong *et al.*, Phys. Rev. Lett. **93**, 080405 (2004).
[56] M. Prager and A. Heidemann, Chem. Rev. **97**, 2933 (1997).