A Langevin canonical approach to the dynamics of chiral systems. Populations and coherences.

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A canonical framework for chiral two–level systems coupled to a bath of harmonic oscillators is developed to extract, from a stochastic dynamics, the thermodynamic equilibrium values of both the population difference and coherences. The incoherent and coherent tunneling regimes are analyzed for an Ohmic environment in terms of a critical temperature defined by the maximum of the heat capacity. The corresponding numerical results issued from solving a non-linear coupled system are fitted to approximate path–integral analytical expressions beyond the so-called non-interacting blip approximation in order to determine the different time scales governing both regimes.

I. INTRODUCTION

The description of many phenomena in terms of a two level system (TLS) can be found in different areas of chemical physics (chiral molecules [1–4]), electron transfer reactions [5, 6], quantum optics [7], high energy physics [8–10] and quantum computation [11], among many others fields of research. However, the isolated TLS is not complex enough to provide a richer and more complete image of the basic microscopic processes underlying its dynamics. For example, very often the system is coupled to a more extended system or environment consisting of many degrees of freedom usually represented by an infinite set of harmonic oscillators. Thus, several extensions of the isolated TLS have been taken into account along the years to account properly for dissipative and stochastic processes due to interactions with an environment at finite temperature. In general, the TLS is linearly coupled to the coordinates of a bath of non-interacting oscillators, whose properties are encoded in their spectral density [12] (the spin–boson model). Several approaches within the matrix density formalism have been proposed and implemented to determine the time evolution of the dissipative TLS such as path-integral methods or the Bloch–Redfield formalism [13–19]. In the path–integral formalism, the so–called non-interacting blip approximation (NIBA) breaks down for non-zero bias and low temperatures even for weak damping, and a theory beyond the NIBA for a biased system has been developed in [20]. Variational calculations have also been carried out for both the symmetric (or unbiased) [20] and asymmetric (or biased) cases [21]. Alternatively, following an approach to the dynamics of the TLS due to Feynman in his elegant dynamical theory of the Josephson effect [22], it was shown that classical and quantum mechanics may be embedded in the same Hamiltonian formulation by using complex canonical coordinates [23, 24]. In particular, for electronically non–adiabatic processes, Meyer and Miller [25] (following some earlier work by McCurdy and Miller [26]) shown the possibility of representing each electronic state by a pair of classical action-angle variables. However, instead of these variables, cartesian electronic variables have been extensively used because of the simpler algebraic form of the Hamiltonian. This approach and some of its extensions have been employed by several groups (for a complete list of references on the development and applications of this method, see [27] and references therein). Furthermore, by using the action–angle variables, this formalism has also been recently implemented to study the dissipative dynamics (zero temperature) of chiral molecules. In this case, the asymmetry of the assumed double well potential model is due to the parity violating energy difference [28–30]. A natural extension of this dynamics is to include the temperature effect along with a noise term.

In this spirit, this is the first of a series of upcoming articles in which we describe, implement and apply a Langevin canonical approach to the dynamics of the chiral TLS interacting with an environment at finite temperatures. Section II is devoted to introduce the canonical formalism for an isolated chiral TLS, as well as its usual connection with the density matrix approach and the corresponding thermodynamics. Finite temperature effects are included by means of noise–induced dynamics via a Caldeira–Leggett–like Hamiltonian. Numerical simulations of this stochastic approach are presented and discussed in Section III, where population differences (which are proportional, for example, to the optical activity in chiral systems [3] [4]) as well as coherences are issued by assuming an Ohmic regime in a broad range of temperatures. In particular, the competition between the tunneling and the asymmetry or bias displayed by the TLS is analyzed in terms of a critical temperature which is defined by the maximum of the heat capacity and separates the coherent and incoherent tunneling regimes. In all cases, these two regimes are discussed in the framework
of a theory beyond the NIBA, path–integral analytical expressions in order to validate this stochastic dynamics. Even more, the corresponding thermodynamic functions are obtained from this stochastic analysis at asymptotic times where the thermal equilibrium is reached. Finally, Section IV presents the main conclusions and future perspectives of the formalism here employed.

II. THEORY

A. A canonical formalism for chiral two level systems

Let us consider an isolated chiral TLS described by the Hamiltonian $\hat{H} = \delta \hat{\sigma}_z + \sigma_z$ where $\sigma_{z,x,y}$ stand for the Pauli matrices. The isolated system is usually modelled in a phenomenological way by a two-well (asymmetric) potential within the Born-Oppenheimer approximation. From the knowledge of the eigenstates, $|1\rangle$ and $|2\rangle$, the left and right states (or chiral states), $|L\rangle$ and $|R\rangle$, respectively, can be expressed by means of a rotation of angle $\theta$ given by $\tan 2\theta = \delta / \epsilon$, where $\langle L|\hat{H}|R\rangle = -\delta$ (with $\delta > 0$) describes the tunneling rate and $2\epsilon = \langle L|\hat{H}|L\rangle - \langle R|\hat{H}|R\rangle$ ($\epsilon$ can be positive or negative) accounts for the asymmetry due to the electroweak parity violation (for a chiral system) or any other bias term (for example, a magnetic field).

Among other interesting representations of the isolated system [31], an alternative and useful way of looking at it is based on the polar decomposition of the complex amplitudes entering the wave function. The solutions of the time-dependent Schrödinger equation ($\hbar = 1$)

$$i \partial_t |\Psi(t)\rangle = \hat{H}|\Psi(t)\rangle$$

(1)

can be written as $|\Psi(t)\rangle = a_L(t)|L\rangle + a_R(t)|R\rangle$. 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 population and phase differences between chiral states are defined as $z(t) \equiv |a_R(t)|^2 - |a_L(t)|^2$ and $\Phi(t) \equiv \Phi_R(t) - \Phi_L(t)$, respectively, it is an easy exercise to prove that the average energy in the normalized $|\Psi(t)\rangle$ state is given by $\langle \Psi|\hat{H}|\Psi\rangle = -2\delta \sqrt{1 - z^2} \cos \Phi + 2\epsilon z \equiv H_0$, where $H_0$ represents a Hamiltonian function. As $z$ and $\Phi$ can be seen as a pair of canonically conjugate variables, the Heisenberg equations of motion (which are formally identical to the Hamilton equations) are easily derived from $\dot{z} = -\partial H_0 / \partial \Phi$ and $\dot{\Phi} = \partial H_0 / \partial z$. Explicitly, the nonlinear coupled equations describing the isolated system in these canonical variables are

$$\dot{z} = -2\delta \sqrt{1 - z^2} \sin \Phi$$

$$\dot{\Phi} = 2\delta \frac{z}{\sqrt{1 - z^2}} \cos \Phi + 2\epsilon.$$  

(2)

Thus, Eqs. (2) are totally equivalent to the usual time-dependent Schrödinger equation (1). In fact, the exact quantum beating expression can be obtained by noting that $H_0$ is a conserved magnitude [28]. For simplicity, the adimensional time $t \rightarrow 2\delta t$ will be used in the rest of this work. This re-scaling implies that the Hamiltonian function $H_0$ is expressed again as

$$H_0 = -\sqrt{1 - z^2} \cos \Phi + \frac{\epsilon}{\delta} z.$$  

(3)

Notice that the first term of the Hamiltonian function accounts for the tunneling process and the second one for the underlying asymmetry (due to a bias or the parity-violating energy difference) putting on evidence the two competing processes in this simple dynamics.

Finally, the connection between the canonical and the density matrix formalism can be established as follows. Let $\hat{\rho}$ be the density matrix for the TLS, whose matrix elements are given by $\rho_{R,R} = |a_R|^2$, $\rho_{L,L} = |a_L|^2$, $\rho_{L,R} = a_L a_R^*$ and $\rho_{R,L} = a_R a_L^*$. On the other hand, from $\langle \Psi(t)|\hat{H}|\Psi(t)\rangle = \text{Tr}(\hat{\rho}\hat{H}) = H_0$, one obtains that the time average values of the Pauli operators are given by

$$\langle \hat{\sigma}_z \rangle_t = \rho_{R,R} - \rho_{L,L} = z$$

$$\langle \hat{\sigma}_x \rangle_t = \rho_{R,L} + \rho_{L,R} = -\sqrt{1 - z^2} \cos \Phi$$

$$\langle \hat{\sigma}_y \rangle_t = i(\rho_{R,L} - i\rho_{L,R}) = -\sqrt{1 - z^2} \sin \Phi,$$

(4)

which is consistent with $\langle \hat{H} \rangle = \delta \langle \hat{\sigma}_z \rangle + \epsilon \langle \hat{\sigma}_z \rangle$ and

$$\langle \hat{\sigma}_z \rangle^2 + \langle \hat{\sigma}_y \rangle^2 + \langle \hat{\sigma}_z \rangle^2 = 1.$$  

(5)

The time population difference can also be split into two components which are symmetric and antisymmetric under the inversion operation consisting of replacing $\epsilon$ by $-\epsilon$.

B. Stochastic dynamics of chiral systems

The dynamics of the isolated chiral TLS can be reduced to simply solve Eqs. (2) and then form appropriate combinations of $z$ and $\Phi$ to recover the populations and coherences. When dealing with interactions with the environment consisting of a high number of degrees of freedom, more sophisticated theoretical approaches are needed. They can be widely classified into three frameworks according to the picture of quantum mechanics used: 1. the density operator formalism and the stochastic Schrödinger equation (Schrödinger and interaction picture), and the generalized Langevin equation (Heisenberg picture). Due to the fact the formalism used here to describe the dynamics of a TLS is very much attached to the definition of a Hamiltonian function [33], the last framework is much more convenient, apart from being much less employed in the theory of open quantum systems. Within this canonical formalism, a Caldeira–Leggett–like Hamiltonian, [12] where a bilinear coupling between the TLS and the environment is assumed, is usually found in the literature. In particular, we have recently developed this formalism to study the dissipative dynamics of chiral systems [28] [30].
As previously stated [28], noting that \( \Phi \) 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–Leggett–like Hamiltonian expressed as

\[
H = H_0 + \frac{1}{2} \sum_i \left( \Lambda_i p_i^2 + \frac{x_i^2 \omega_i^2}{\Lambda_i} \right) - \Phi \sum_i c_i x_i + \Phi^2 \sum_i c_i^2 \Lambda_i, \tag{6}
\]

where the sums run over the coordinates of the bath oscillators \( \{p_i, x_i\} \) and \( \Lambda_i, c_i \) and \( \omega_i \) are suitable dimensionless constants representing generalized masses, couplings with the environment, and oscillator frequencies, respectively. Although the requirement of a bilinear coupling has been relaxed in a previous publication [30], it will be retained here for simplicity.

It should also be noticed that the usual spin–boson Hamiltonian has been implemented in the Meyer–Miller–Stock–Thoss representation by coupling the bath position coordinate with the population difference of the TLS [5]. This phase difference is coupled to the degrees of freedom of the bath which also acts as a source of phase fluctuations.

Within this scheme, the corresponding coupled Langevin-type dynamical equations are given by

\[
\dot{z} = -\sqrt{1 - z^2} \sin \Phi - \int_0^t \gamma(t-t') \Phi(t') \dot{\Phi}(t') \, dt' + \xi(t) \tag{7a}
\]

\[
\dot{\Phi} = \frac{z}{\sqrt{1 - z^2}} \cos \Phi + \frac{\xi}{\delta}, \tag{7b}
\]

where the time-dependent friction (damping kernel) is expressed as

\[
\gamma(t) = \sum_i \Lambda_i c_i^2 \cos \omega_i (t - t') \tag{8}
\]

and the fluctuation force or noise is given by

\[
\xi(t) = \sum_i c_i \Lambda_i \left( x_i(0) \cos \omega_i t + p_i(0) \sin \omega_i t \right) - c_i^2 \Lambda_i \Phi(0) \cos \omega_i t \tag{9}
\]

which depends on the initial conditions of both the system and the bath. Taking the bath oscillators as classical variables (classical noise), moderate–to–high temperature regimes are expected to be properly described by this approach, as will be discussed through the rest of the manuscript.

If a Markovian regime is assumed, the standard properties of the fluctuation force (Gaussian white noise) are given by the following canonical thermal averages:

\[
\langle \xi(t) \rangle_\beta = 0 \text{ (zero average)} \quad \text{and} \quad \langle \xi(0) \xi(t) \rangle_\beta = mk_B T \gamma \delta(t) \text{ (delta-correlated)} \quad \text{where} \beta = (k_B T)^{-1}, \text{ } k_B \text{ being Boltzmann’s constant.} \]

The friction is then described by \( \gamma(t) = 2 \gamma \delta(t) \), where \( \gamma \) is a constant and \( \delta(t) \) is Dirac’s \( \delta \)-function (not to be confused with the \( \delta \)-parameter describing the tunneling rate). Thus, in this regime, Eqs. (7) read now

\[
\dot{z} = -\sqrt{1 - z^2} \sin \Phi - \gamma \dot{\Phi}(t) + \xi(t) \tag{10a}
\]

\[
\dot{\Phi} = \frac{z}{\sqrt{1 - z^2}} \cos \Phi + \frac{\xi}{\delta} \tag{10b}
\]

The corresponding solutions provide stochastic trajectories for the population and phase differences encoding all the information on the dynamics of the non-isolated TLS. These solutions are dependent on the four dimensional parameter space \((\epsilon, \delta, \gamma, T)\), apart from the initial conditions \(z(0) = z_0\) and \(\Phi(0) = \Phi_0\). In terms of the averages of Pauli operators, we have now the condition

\[
\langle \sigma_x \rangle^2 + \langle \sigma_y \rangle^2 + \langle \sigma_z \rangle^2 < 1. \tag{11}
\]

instead of condition (5).

The use of classical noise imposes some restrictions on the range of temperatures where this approach remains valid. At high temperatures, \( \beta^{-1} \gg h \gamma \) (or \( \gamma^{-1} \gg h \beta \)) thermal effects are going to be predominant over quantum effects which become relevant, in general, at times of the order of or less than \( h \beta \), sometimes also called thermal time. However, in general, at very low temperatures, \( \beta^{-1} \ll h \gamma \) (or \( \gamma^{-1} \ll h \beta \)) the noise is colored and its correlation function is complex and our approach is no longer valid. The dissipative dynamics in the classical noise regime is obtained at zero noise or zero temperature [34]. This regime has already been considered elsewhere [30].

Canonical thermal averages of population and phase differences as a function of time \( \langle z(t) \rangle_\beta \) and \( \langle \Phi(t) \rangle_\beta \) are issued from running a high number of stochastic trajectories. The role of initial conditions has been extensively discussed in the literature (see, for example, [3, 32]) and we are not going to deal with this important issue. In our dynamical study, the system will be prepared in one of the chiral states, left or right \((z_0 = 0.999 \text{ or } -0.999)\) in order to avoid initial singularities, and the initial phase difference \(\Phi_0\) will be uniformly distributed around the interval \([-2\pi, 2\pi]\). This approach should recover the main equilibrium thermodynamics properties of the non-isolated TLS from the stochastic dynamics at asymptotic times.

### C. Thermodynamics of chiral two-level systems

A detailed analysis of the thermodynamics of non-interacting chiral molecules assuming a canonical distribution was carried out elsewhere [32]. In particular, thermal averages of pseudoscalar operators were extensively analyzed. The canonical thermal average of
an observable $X$ is defined as $\langle X \rangle_\beta = \text{Tr}(\rho_\beta X)$ where $\rho_\beta = Z^{-1} e^{-\beta H_0}$, $H_0$ is given by (3) and $Z$ is the partition function. For chiral states, $Z = 2 \cosh(\beta \Delta)$ with $\Delta = \sqrt{\beta^2 + \epsilon^2}$ and the corresponding averages for the population difference and coherences (in the L–R basis) are then calculated to give

$$\langle z \rangle_\beta \equiv \langle \hat{\sigma}_z \rangle_\beta = \frac{\epsilon}{\Delta} \tanh(\beta \Delta)$$

$$\langle \hat{\sigma}_x \rangle_\beta = \frac{\delta}{\Delta} \tanh(\beta \Delta)$$

(12)

From the knowledge of the partition function, the remaining equilibrium thermodynamical functions are also derived when $\langle z \rangle$ is determined by the competition between tunneling and asymmetry or bias. At temperatures higher than $T_c$, the effect of $\epsilon$ is masked by thermal effects which tend to wash out the critical temperature given by (35). Notice that in the Langevin–like coupled equations to be solved, the noise term only appears in the equation of motion of the $z$–variable. The phase variable has been taken to be uniformly distributed between $-2\pi$ and $2\pi$.

In order to avoid the singular behavior found at $z \to \pm 1$, the initial value for $z$ will be chosen to be around $\pm 0.999$, very far from the equilibrium condition. Moreover, when running trajectories there are some of them visiting “unphysical” regions, that is, $|z| > 1$. This drawback is mainly associated with the intensity of the noise since, for large values of it (which depends on both the temperature and the friction coefficient), the stochastic $z$–trajectories can become unbounded. To overcome this problem, we have implemented a reflecting condition such that, for instance, when the trajectory reaches $z > 1$, we change its value to $2 - z$. The time step used goes from $10^{-6}$ to $10^{-4}$ (dimensionless units) depending strongly on the regime to be explored in order to follow properly the corresponding dynamics: high or moderate temperature regimes and localized or delocalized regimes. As noted in (38), unstable trajectories can also be found for certain values of $\epsilon$, $\delta$ and $\gamma$ in the simple case of dissipative but non–noisy dynamics. As this problem persists in case of dealing with stochastic trajectories, not every triple $(\epsilon, \delta, \gamma)$ gives place to a stable trajectory. In these cases, the time evolution of individual trajectories is not possible and a previous stability analysis is mandatory. However, in the stable case, a satisfactory description of population differences and coherences has been achieved by running up to $10^4$ trajectories in all cases considered.

### B. Population differences and coherences

In this subsection, thermal effects both in the population difference and coherences will be studied, extending previous results in which only dissipative dynamics (that is, at zero temperature) was considered (39). Specifically, we will focus on the role of the critical temperature such that, roughly speaking, separates coherent from incoherent tunneling. Regarding the internal dynamics of the TLS, we start analyzing the delocalized regime where $\delta > \epsilon$. In particular, we have taken $\delta = 1$ and $\epsilon = 0.5$. Given these values, the critical temperature is $T_c \sim 1$ in units of $\Delta$. Thus, to study its effects in the dynamics, temperatures ranging from $200$ to $0.4$ (in units of $\Delta$) have been considered. As the friction has been taken to be a constant value, $\gamma = 0.1$, both moderate and high temperature regimes ($k_B T \sim 1/2\pi$ and $k_B T \gg h\gamma$, respectively) are covered. The propagation time step has been taken to be between $10^{-6}$ (high temperatures) and $10^{-4}$ (moderate temperatures).

Trajectory averages (black dashed curves) of the population differences, $\langle z(t) \rangle_\beta$, are plotted in Fig. (1) for the range of temperatures previously given above. Left panels ($a$, $c$ and $e$) show calculations for $T = 200, 20$ and

### III. RESULTS

#### A. Numerical details

The general strategy consist of solving the pair of nonlinear coupled equations (10) for the canonical variables under the action of a Gaussian white noise, which is implemented by using an Ermak–like approach (38, 39). Notice that in the Langevin–like coupled equations to be solved, the noise term only appears in the equation of motion of the $z$–variable. The phase variable has been taken to be uniformly distributed between $-2\pi$ and $2\pi$. In order to avoid the singular behavior found at $z \to \pm 1$, the initial value for $z$ will be chosen to be around $\pm 0.999$, very far from the equilibrium condition. Moreover, when running trajectories there are some of them visiting “unphysical” regions, that is, $|z| > 1$. This drawback is mainly associated with the intensity of the noise since, for large values of it (which depends on both the temperature and the friction coefficient), the stochastic $z$–trajectories can become unbounded. To overcome this problem, we have implemented a reflecting condition such that, for instance, when the trajectory reaches $z > 1$, we change its value to $2 - z$. The time step used goes from $10^{-6}$ to $10^{-4}$ (dimensionless units) depending strongly on the regime to be explored in order to follow properly the corresponding dynamics: high or moderate temperature regimes and localized or delocalized regimes. As noted in (38), unstable trajectories can also be found for certain values of $\epsilon$, $\delta$ and $\gamma$ in the simple case of dissipative but non–noisy dynamics. As this problem persists in case of dealing with stochastic trajectories, not every triple $(\epsilon, \delta, \gamma)$ gives place to a stable trajectory. In these cases, the time evolution of individual trajectories is not possible and a previous stability analysis is mandatory. However, in the stable case, a satisfactory description of population differences and coherences has been achieved by running up to $10^4$ trajectories in all cases considered.
The internal energy scale of the TLS (roughly given by $\delta$ and $\epsilon$) the competition between the thermal and coherent tunneling process dominates the dynamics (remembering that at lower temperatures, the coherent tunneling which prevails at the two highest temperatures analyzed (panels a and b) leads to racemization very rapidly. When the temperature approaches the critical temperature, $T_c$, (panels d and e) the competition between the thermal and the internal energy scale of the TLS (roughly given by $k_B T$ and $\hbar \Delta$, respectively) gives place to the appearance of the oscillating profile, fingerprint of coherent tunneling. When the temperature is again lowered (panel f), the dynamics which defines the coherent–incoherent transition.

In order to extract more physical information from our approach, these stochastic calculations are fitted to analytical expressions describing both coherent and incoherent tunneling. In the weak Ohmic damping limit and moderate–to–high temperature regime the path-integral results (beyond the NIBA framework) show a dependence on time according to
\[
\langle z(t) \rangle_\beta = \langle z \rangle_\beta + [1 - \langle z \rangle_\beta] e^{-\gamma t},
\]
for the incoherent regime and
\[
\langle z(t) \rangle_\beta = a_1 e^{-\gamma_1 t} + \langle z \rangle_\beta + [(1 - a_1 - \langle z \rangle_\beta) \cos \Omega t + a_2 \sin \Omega t] e^{-\gamma t},
\]
for the coherent regime. In these two equations, $\gamma_2, a_1, a_2, \gamma_1, \gamma, \Omega$ are considered as free parameters and $\langle z \rangle_\beta$ is given by the first expression of Eq. (12). Notice the fairly good fittings of the average of the stochastic trajectories to Eqs. (14) and (15) (displayed by dashed red lines) for all panels of Fig. 1. $\Omega$ can be interpreted as the oscillation frequency of an effective damped harmonic oscillator (Rabi-type) and $\gamma_1, \gamma_2$ and $\gamma$ the different relaxation rates in this very involved dynamics. In particular, $\gamma_2$ gives the effective decay rate for the incoherent tunneling and $\gamma_1$ and $\gamma$ two effective decays for the coherent tunneling with different weights. In other words, for this last regime, $\Omega$ and $\gamma$ give us globally the two different time scales observed in this stochastic dynamics since $\gamma_1$ gives the incoherent contribution in this coherent regime. All of these parameters are related by quite cumbersome expressions according to the path-integral method. The quality of the fitting should be related to the right behavior underlying by the stochastic trajectories.

![Figure 1](image1.png)

**Figure 1.** Time dependence of $\langle z(t) \rangle_\beta$ for different temperature values (in units of $\Delta$): (a) 200, (b) 40, (c) 20, (d) 4, (e) 2 and (f) 0.4. Black dashed curves are issued from solving Eqs. (10) and red dashed curves from Eqs. (12) (incoherent regime) and (13) (coherent regime).

![Figure 2](image2.png)

**Figure 2.** Time dependence of the coherence $\langle \hat{\sigma}_x \rangle_\beta$ for different temperature values (in units of $\Delta$): (a) 200, (b) 40, (c) 20, (d) 4, (e) 2 and (f) 0.4. Black dashed curves are issued from solving Eq. (10) and red dashed curves from Eq. (13). For simplicity in the legend of the vertical axis, the hat of the Pauli operator in the $x$-direction has been removed.

Let us consider now coherences. However, instead of analyzing the average values of the phase difference given...
Table I. Numerical fitting of the average of stochastic trajectories corresponding to population differences and coherences (Eqs. 15 and 16). For simplicity, only \( T = 4 \) and 40 and certain values of the ratio \( \epsilon/\delta \) are shown. All the quantities are dimensionless.

| \( T \) | \( \epsilon/\delta \) | \( \gamma_1 \) | \( \Omega \) | \( \gamma \) |
|-----|-------|-------|------|------|
| (\( \Phi \)) | 4 | 0.5 | 0.0164 | -1.120 | 0.015 |
| (\( \Phi' \)) | 4 | 0.5 | 0.0162 | -1.120 | 0.015 |
| (\( \Phi'' \)) | 4 | 1.0 | 0.2010 | -1.410 | 0.013 |
| (\( \Phi''' \)) | 4 | 1.0 | 0.2000 | -1.410 | 0.012 |
| (\( \Phi^{(4)} \)) | 40 | 1.5 | 0.1220 | -1.800 | 0.067 |
| (\( \Phi^{(5)} \)) | 40 | 1.5 | 0.1220 | -1.798 | 0.072 |
| (\( \Phi^{(6)} \)) | 40 | 1.0 | 0.1060 | -1.407 | 0.069 |
| (\( \Phi^{(7)} \)) | 40 | 1.0 | 0.1160 | -1.408 | 0.076 |

by \( \langle \Phi(t) \rangle_\beta \), we have calculated the thermal average value of \( \langle \hat{\sigma}_x(t) \rangle_\beta \) issued from our stochastic trajectory analysis from the second expression of Eq. (14). These values are plotted in Fig. 2 for the same temperature values as reported in Fig. 1 (the same temperature value is assigned to each panel). Thus, we are considering \( \langle \hat{\sigma}_x(t) \rangle = (-\sqrt{1-z^2} \cos \Phi) \) and the stochastic behavior on time is given by the black dashed curves, as before. Similar comments with respect to the incoherent and coherent regimes are also applicable here. Even more, in the weak Ohmic damping limit and moderate-to-high temperature regime our stochastic values are again fitted to the corresponding expression provided by the path-integral method according to [2]

\[
\langle \hat{\sigma}_x \rangle(t) = b_1 e^{-\gamma t} + \langle \hat{\sigma}_x \rangle_\beta \\
+ \left[ (b_1 + \langle \hat{\sigma}_x \rangle_\beta) \cos \Omega t + b_2 \sin \Omega t \right] e^{-\gamma t},
\]

where \( b_1, b_2 \) are again taken as free parameters and \( \langle \hat{\sigma}_x \rangle_\beta \) is given by the second expression of Eqs. (12). As before, the same interpretations of \( \Omega, \gamma_1 \) and \( \gamma \) are pertinent.

The consistency of the fittings in Figs. 1 and 2 is supported by the obtention of identical numerical values for those parameters which are common to both expressions in Eqs. (15) and (16). This is illustrated in Table I for only two temperatures, \( T = 4 \) and \( T = 40 \). The different time scales clearly manifest in such a table.

C. Thermodynamics from stochastic dynamics

Finally, it should be noticed that the formalism here presented describes rather accurately the time dependence of both the population differences and coherences, being an alternative way to solve the time-dependent Schrödinger equation. It is also worth noting the capabilities of this approach to describe properly equilibrium thermodynamics in a large interval of temperatures, ranging from moderate to high ones. In the very low-temperature regime, where \( k_B T \ll h\gamma \), quantum noise effects are expected to occur. In this regime, the non-commutativity of the canonical variables describing the bath, \( [x_i, p_i] \neq 0 \), would lead to \( \sigma_i(t), \xi(t') \neq 0 \). Thus, within this range of temperatures, the approximation here employed should break up. However, in our study, we have assumed that the thermodynamical behavior at low temperatures is also described by a canonical distribution and correct values should also be obtained under this assumption.

Having in mind this limitation, we note that classical noise effects properly describe the region where both thermal and internal effects driving the dynamics of the TLS take place (in particular, for temperatures close to \( T_c \)). In addition, the effects of the delocalization/localization (given by the ratio between \( \delta \) and \( \epsilon \)) are correctly taken into account, as can be seen in Figs. 3 and 4. In these two figures, the thermodynamical functions given by Eqs. (12) are plotted (solid lines) for the two main regimes studied: \( \epsilon > \delta \) (Fig. 3), and \( \epsilon < \delta \) (Fig. 4). Similar results have also been obtained for the regime \( \epsilon \sim \delta \). The black points in both sets of figures are the time asymptotic values issued from the stochastic dynamics. As can be seen, the agreement is fairly good at all temperatures studied. Thus, we can conclude that both the localized and delocalized regimes are correctly described by the approach here presented. Clearly, the thermodynamical behavior is independent on the friction value chosen.
IV. CONCLUSION

In this work, a Langevin canonical approach has been developed to study the thermodynamics of chiral two-level systems interacting with a thermal bath. Thermal effects due to a noisy environment, modelled as a collection of classical harmonic oscillators coupled linearly with the system via a Caldeira–Leggett–like Hamiltonian have been taken into account. The canonical variables have been related to both the population differences and coherences of the system, showing that complete information about the dynamics can be encoded in them. The competing localization/delocalization process which is governed by the tunneling and the asymmetry of the TLS has been analyzed in terms of the critical temperature for an Ohmic environment. In particular, we have shown that this critical temperature separates the incoherent and coherent tunneling regimes. A high number of stochastic trajectories have been carried out in order to provide time-dependent canonical thermal averages of the population differences and coherences, showing that the implementation of the noise term in the dynamics is properly accounted for. This approach has allowed us to follow the evolution of the system towards the thermodynamic equilibrium with fairly good accuracy. Moreover, these stochastic results have been fitted to analytical expressions beyond the NIBA to extract more physical information of the parameters ruling this dynamics such as global damping coefficients as well as Rabi-type frequencies. The regime of very low temperatures (much smaller than the critical temperature) which requires a generalized Langevin equation is not considered.

As has been recently reported by Miller [40], an important topic in particle dynamics is to ascertain the origin of coherence, classical or quantum, caused by interference of probability amplitudes. One of the concluding remarks was that sometimes whether coherence is quantum or classical depends on what is being observed. When speaking about observation, one has to think in terms of a measurement apparatus. It is well known that an environment can be seen as this apparatus [5]. When interacting with the system, it displays decoherence. In our case, the system always displays tunneling (a typical quantum feature) but the environment which has been considered to be classical leads to decoherence. However, coherence at short times is still observed when the temperature and the friction are small. Thus, in this context, we deal with the classical observation of quantum coherence which is destroyed at asymptotic times.

An extension of this work including correlation functions and more thermodynamics functions such as heat capacity and entropy as well as the introduction of a magnetic field is currently in progress.

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[1] Harris RA, Stodolsky L. Quantum beats in optical activity and weak interactions. Phys. Lett. B 1978; 78: 313–317.
[2] Quack M. On the measurement of the parity violating energy difference between enantiomers. Chem. Phys. Lett. 1986; 132: 147–153.
[3] MacDermott AJ, Hegstrom RA. A proposed experiment to measure the parity-violating energy difference between enantiomers from the optical rotation of chiral ammonia-like "cat" molecules. Chem Phys 2004; 305: 55–68.
[4] MacDermott AJ. Chiroptical signatures of life and fundamental physics. Chirality 2012; 24: 764–769.
[5] Weiss U. Quantum dissipative systems (2nd edn.). Singapore: World Scientific; 1999. 448 p.
[6] Volkhard M, Kühn O. Charge and energy transfer dynamics in molecular systems (2nd edn.). Weinheim: Wiley-VCH; 2004. 562 p.
[7] Scully MO, Zubairy MS. Quantum optics. Cambridge: Cambridge University Press; 1997. 630 p.
[8] Rosner JL, Slezak SA. Classical illustrations of CP violation in kaon decays. Am J Phys 2001; 69: 44–49.
[9] Capozziello S, Lattanzi. Quantum mechanical considera-
tions on the algebraic structure of central molecular chirality. Chirality 2004; 16:162-167.

[10] Capozziello S, Lattanzi. Chiral tetrahedrons as unitary quaternions. Molecules and particles under the same standard. Int. J. Quant. Chem. 2005; 104: 885-893

[11] Ladd TD, Jelezko F, Laflamme R, Nakamura Y, Monroe C, O'Brien JL. Quantum computers. Nature 2010; 464: 45–53.

[12] Leggett AJ, Chakravarty S, Dorsey AT, Fisher MP, Matthew PA, Garg A and Zwerger W. Dynamics of the dissipative two-state system. Rev Mod Phys 1987; 59: 1–85.

[13] Redfield AG, On the Ttheory of relaxation processes. IBM J Res Dev 1957; 1: 19–31.

[14] Senitzki IR. Dissipation in quantum mechanics. The two-level system. Phys Rev 1963; 131: 2827–2838.

[15] Harris RA, Stodolsky L. On the stabilization of optical isomers through tunneling friction. J Chem Phys 1983; 78: 7330–7334.

[16] Vincenzo DP, Loss D. Rigorous Born approximation and beyond for the spin-boson model. Phys Rev B 2005; 71: 035318–035328.

[17] Bargueño P, Peñate–Rodríguez HC, Gonzalo I, Sols F, Miret–Artes S. Friction-induced enhancement in the optical activity of interacting chiral molecules. Chem Phys Lett 2011; 516: 29–34.

[18] Sanz AS, Miret–Artes S. A trajectory description of quantum processes. I. Fundamentals. Lecture Notes in Physics 2012; 850: 1–300.

[19] Bargueño P, Gonzalo I, Pérez de Tudela R, Miret–Artes S. Parity violation and critical temperature of noninteracting chiral molecules. Chem Phys Lett 2009; 483: 204–208.

[20] Bargueño P, Pérez de Tudela R, Miret–Artes S, Gonzalo I. An alternative route to detect parity violating energy difference through Bose-Einstein condensation of chiral molecules. Phys Chem Chem Phys 2011; 13: 806–810.