Entropy dynamics for a propeller-shaped quantum Brownian molecular rotator

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Abstract: We investigate and analyze the time dependence of the so-called differential entropy as a measure of the dynamical stability of a one-dimensional, propeller-shaped quantum Brownian molecular rotator. The larger the entropy change, the more profound the instability (lower control) of the rotator. The quantum molecular rotator is modelled by the quantum Caldeira-Leggett master equation while assuming the external harmonic field for the rotator. Rotational stability is found relatively high for the constructed Gaussian states, especially for molecules with a larger number of blades.

Keywords: molecular cogwheels, entropy, open quantum systems, Brownian motion

1. Introduction

Achieving the goals of molecular nanotechnology requires a multidisciplinary approach [1-4]. Theoretical results are often instrumental for applications. The propeller-shaped molecular rotators (molecular cogwheels) are among the basic elements of molecular nanomachinery [1-5]. Exposed to the environmental influence, molecular cogwheels (MC) exhibit stochastic, dynamically unstable behavior; in general, the molecules suffer from decoherence, diffusion, friction, state relaxation or even thermalization [1-6]. The expected realistic situations are characteristic of the short and rather frequent external actions applied on the rotator thus raising a question of the possibly non-negligible quantum-mechanical corrections (much before the possible relaxation or thermalization of the rotator). Only recently similar analyzes have been systematically performed [7-13]. The nonexistence of a canonical quantifier imposes the task of comparing the different methods of statistical inference in order to improve stability and therefore the desired dynamical control of the molecular rotators [1-3,8,11].

In this paper, we perform an analysis of the MC dynamical stability via the use of *entropy*. To this end, entropy as a quantifier of information is not very informative per se [14]. The larger the *change* of entropy the less stable—the less predictable, and therefore the less controllable—are the molecular rotations. We utilize a quantum model of the

Brownian motion [6,15] for small rotations of a propeller-shaped molecule while assuming that the molecule is exposed to a constant external harmonic field.

2. Model and methods

The so-called Caldeira-Leggett (CL) master equation is a proper quantum-mechanical counterpart of the classical Brownian motion model [6,15]. It is suited well also for investigating the dynamics of a planar rotator with the assumption of a very small angle of rotation [8,11]. Interestingly, it is possible to account for the *size* of the propeller-shaped molecules by re-scaling the molecule moment of inertia ($I = nI_0$) and the so-called damping factor ($\gamma = n\gamma_0$) for a molecule with the number n of blades [8,11]. Denoting the angle of rotation by φ and the angular momentum by L, the CL master equation in the Schrodinger picture and in the position representation reads [6,8,11]:

$$\frac{\partial\rho(\varphi,\varphi',t)}{\partial t} = \left[\frac{i\hbar}{2nI_0}\left(\frac{\partial^2}{\partial\varphi^2} - \frac{\partial^2}{\partial\varphi'^2}\right) - \frac{i}{\hbar}\left(V(\varphi) - V(\varphi')\right) - n\gamma_0(\varphi-\varphi')\left(\frac{\partial}{\partial\varphi} - \frac{\partial}{\partial\varphi'}\right) - \frac{2n^2I_0\gamma_0kT}{\hbar^2}(\varphi-\varphi')^2\right]\rho(\varphi,\varphi',t), \quad (1)$$

where I_0 is the average moment of inertia and γ_0 the average damping factor for the set of n blades, while k is the Boltzmann's constant, T is the environment temperature and the external field $V(x)$. The unknown function is the so-called "kernel" of the "density matrix" (statistical operator) $\hat{\rho}(t)$, $\rho(\varphi,\varphi',t) \equiv \langle\varphi|\hat{\rho}(t)|\varphi'\rangle$, which for $\varphi = \varphi'$ becomes the probability distribution $\rho(\varphi,t)$.

The general solution to equation (1) is not known. The process described by equation (1) is known to have a (dynamically inaccessible) *stationary state*, $\hat{\rho}(t) = \int d\varphi\, d\varphi' \rho(\varphi,\varphi',t)|\varphi\rangle\langle\varphi'|$, with the kernel [6]:

$$\rho(\varphi,\varphi',t) = \frac{1}{\sqrt{\sigma_\varphi^2 2\pi}} exp\left\{-\frac{1}{2\sigma_\varphi^2}\left(\frac{\varphi+\varphi'}{2}\right)^2 - \frac{\sigma_L^2}{2\hbar^2}(\varphi-\varphi')^2\right\} \quad (2)$$

for the external harmonic potential $V(\varphi) = nI_0\omega^2\varphi^2/2$ and the circular frequency ω, while by σs we denote the standard deviations.

On the other hand, the approximate stationary state(s) may produce the least change of entropy. That is, preparation of the rotator in that state is expected to lead to a relatively stable rotation. Hence, we "equip" the time-independent stationary state (2) with the following *ansatz*: instead of the time-independent standard deviations σ_φ^2 and σ_L^2, in equation (2), we place the known time-dependent standard deviations [8],

$$\sigma_\varphi^2(t) = e^{-2n\gamma_0 t}\left(\sigma_\varphi^2(0)(\cos\omega t)^2 + \frac{\sigma_L^2(0)}{(nI_0\omega)^2}(\sin\omega t)^2 + \frac{\sigma(0)}{2nI_0\omega}\sin 2\omega t\right) + \frac{kT}{nI_0\omega^2}(1 - e^{-2n\gamma_0 t}),$$

$$\sigma_L^2(t) = e^{-2n\gamma_0 t}\left(\sigma_L^2(0)(\cos\omega t)^2 + (nI_0\omega)^2\sigma_\varphi^2(0)(\sin\omega t)^2 - \frac{nI_0\omega}{2}\sigma(0)\sin 2\omega t\right) + nI_0kT\,(1 - e^{-2n\gamma_0 t}), \quad (3)$$

where $\sigma(0)$ is the initial value of the correlation between the angle and the angular momentum. Now, we can calculate the time change of entropy.

3. Results

For the "equipped" initial states, we perform study of the so-called *differential*

entropy, S_d, that is defined as [16]:

$$S_d(t) = -\int d\varphi\, \rho(\varphi, t) \ln \rho(\varphi, t), \quad (4)$$

with the range $\varphi \in [-\pi, \pi]$ of integration.

The results for the absolute value of the relative change of entropy (quantum versus classical), $\delta S_d = |(S_d(t) - S_d(0))/S_d(0)|$, are graphically presented in Figure 1 for small angle of rotation (i.e., small time interval $t \in [0,0.1]$). The rotator/bath parameters are chosen: $\sigma_\varphi(0) = 0.1, \sigma_L(0) = 10, \sigma(0) = 0, \gamma_0 = 0.001, \omega = 1, kT = 10, I_0 = 1 = \hbar$.

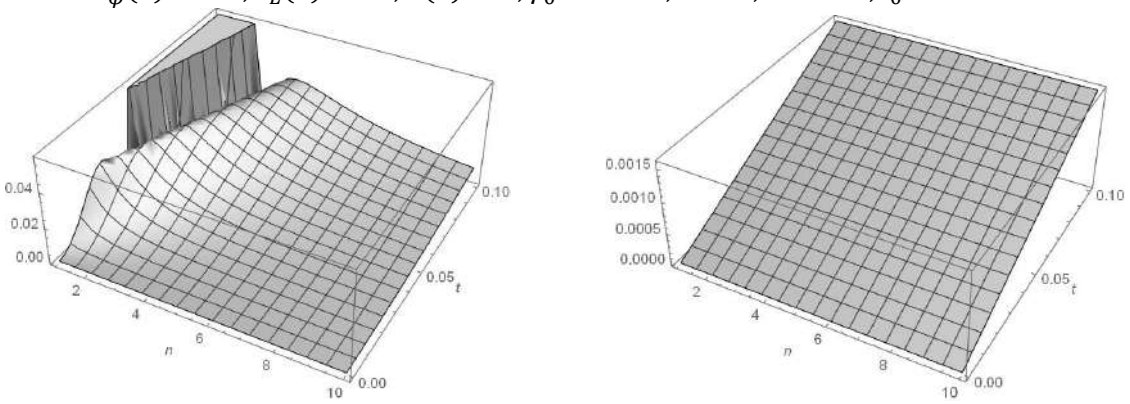

Figure 1. Time change of the absolute value of the relative differential entropy δS_d: (left) quantum and (right) classical case. The classical expression follows from the classically allowed zero standard deviations in equation (3).

3. Conclusions

From Figure 1, we can detect both relatively stable rotation ($\delta S_d \sim 0.15 - 4\%$ for $n > 1$) and significant quantum contributions already for short time intervals for the underdamped regime ($kT = 10$). Better dynamical stability is found for larger number n of blades for the quantum case. Overall, small change of δS_d even for the quantum case is encouraging in search for better stability of the molecular rotations – that deserves more detailed and comprehensive study to be presented elsewhere [17].

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