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The role of size and shape in the stability of the quantum Brownian rotator

Igor Petrović [a,*], **Jasmina Jeknić-Dugić** [a], **Momir Arsenijević** [b], **Miroljub Dugić** [b], **Saša Gocić** [a]

[a] *University of Niš, Faculty of Science and Mathematics, Višegradska 33, 18000 Niš, Serbia*

[b] *University of Kragujevac, Faculty of Science, Radoja Domanovića 12, 34000 Kragujevac, Serbia*

E-mail: igorpetrovicsb@gmail.com, jjeknic@pmf.ni.ac.rs, fajnman@gmail.com, mdugic18@sbb.rs, sasa.gocic@pmf.edu.rs

Shape and size are the basic characteristics of macroscopic, classical systems, and as such represent a special challenge within the fundamental problem of "transition from quantum to classical", but also the problem of quantum measurement. Propeller-shaped molecules are excellent candidates for analyzing the effects of size and shape because of the linear dependence of both the moment of inertia and the damping factor on the number of propeller blades. Also, such research can be useful for their practical application within molecular machines technology. The obtained results indicate a very complex dependence of dynamic stability on the size of the system, as well as some unexpected characteristics of the time evolution of standard deviations in some cases. The new method called "the quantum first passage time" also led to unexpected conclusions, just like the analysis of the role of decoherence in the transition from quantum to classical behavior.

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[*] Speaker

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1. Introduction

The interplay of the quantum mechanical and classical dynamics of quantum systems is closely related to the problem of the "transition from the quantum to the classical world", as well as to the problem of quantum measurement, which is one of the biggest conceptual problems of quantum mechanics. In this context, it is useful to consider the effect of the size of physical systems and to study systems whose size is close to the assumed boundary of the quantum and classical domains. Notable examples of such systems are molecules, especially large ones. A particularly interesting question is the very existence of a certain size and shape of these molecules. They are often assumed to have definite shapes, although, according to the rules of quantum mechanics, molecules would have to be in the superposition of multiple possible shapes. A definite shape and size are characteristics of classical physical systems, which means that molecules, although they are primarily quantum objects, also exhibit some classical properties.

There is still no general quantum theory which connects system dynamics with spatial magnitude, nor with system geometry. Standard quantum mechanical theory is insensitive to the number of particles, that is, to the number of degrees of freedom, or, more intuitively, to the size of the physical system. However, if the physical system is considered open, the interaction with the environment is expected to be determined by both its size and shape. The larger the system, the stronger interaction with the environment. In addition, according to the general quantum decoherence theory, it can be expected that the environment effectively distinguishes different shapes of molecules. To this end, molecular rotators are almost ideal candidates. Especially interesting is their role in modern nanotechnology and their application as components of artificial molecular machines [1,2]. For certain parts of the molecular machines, it is very important to have a specific shape, as well as a specific size so as to perform the intended function. The functioning of molecular machines requires a high degree of control over the relative motion of its constituent parts, and in some cases the motion of the machine as a whole. By controlling the translational and rotational movements of the machine components, it is possible to achieve a predetermined function. From a formal point of view, the control assumes dynamical stability of the molecule dynamics. Realistic molecules are open, i.e., interacting with the surrounding environment and thus subject to different effect, such as the Brownian motion. Therefore, as an important task appears a theoretical study of the size-and-shape dependence of the quantum Brownian effect.

2. The model

Molecular rotators can be modeled by a single (rotational) degree of freedom as a rigid system that is open to environmental influence using the so-called Caldeira-Leggett master equation [3] that, for the case of a plane rotator in the external field $\hat{V}(\varphi)$, can be written in the form:

$$\frac{d}{dt}\hat{\rho}_R(t) = -\frac{i}{\hbar}\left[\hat{H}_R, \hat{\rho}_R(t)\right] - \frac{i\gamma}{\hbar}\left[\hat{\varphi}, \left\{\hat{L}_z, \hat{\rho}_R(t)\right\}\right] - \frac{2I\gamma k_B T}{\hbar^2}\left[\hat{\varphi}, \left[\hat{\varphi}, \hat{\rho}_R(t)\right]\right], \qquad (1)$$

where:

$$\hat{H}_R = \frac{\hat{L}_z^2}{2I} + \hat{V}(\hat{\varphi}), \tag{2}$$

is the rotator's self-Hamiltonian, while γ is the damping factor, k_B is the Boltzmann constant, T is the temperature of the thermal bath, $\hat{\rho}_R$ statistical operator (density matrix) which describes the state of the Brownian rotator. Transition from the translational to the rotational Brownian model is formally straightforward for small angles of rotation: the position operator is exchanged by the angle of rotation $\hat{\varphi}$, momentum by the angular momentum $\hat{L}_z$, and the mass by the rotator's moment of inertia I. The use of this equation is motivated by both, the well-defined classical limit as well as by the explicit quantum mechanical corrections in the weak-coupling limit. We use this equation phenomenologically, i.e. without limiting the parameters that were taken into account during its microscopic derivation (weak interaction with the environment, i.e. a small damping factor, as well as high temperature), which enables its application in a wider range of values of the relevant quantities.

In many real-world physical situations, the Brownian rotator is, in addition to the constant influence of Brownian motion, under the influence of external fields. In most cases, this external field can be considered harmonic, or weakly unharmonic, i.e. with a small cubic term. Accordingly, in this paper, the following rotator models are tested and mutually compared: free rotator (out-of-field), rotator in a (effective) harmonic external field for which the potential is:

$$\hat{V}(\hat{\varphi}) = \frac{1}{2} I\omega^2 \hat{\varphi}^2, \tag{3}$$

where ω is the angular frequency of the rotator, and the rotator in a weakly unharmonic external field:

$$\hat{V}(\hat{\varphi}) = \frac{1}{2} I\omega^2 \hat{\varphi}^2 + b\hat{\varphi}^3, \tag{4}$$

where b is a small constant.

A particularly interesting type of molecular rotators are the so-called molecular propellers, which consist of several atomic groups that are attached to one atomic group located in the center, so that the whole formation looks like propellers. In molecular propellers, the shape itself is what characterizes their application and function. They can be used in so-called molecular gears, i.e. they can be interconnected with other propellers. What makes molecular propellers the best candidates for analyzing the influence of size and shape on dynamic stability is the fact that it is easy and simple to quantify their size by the number of blades they consist of. If we observe one group of molecular propellers having the same or similar group of atoms in its central part and the same or similar group of atoms representing the blades, then we can say that the total moment of inertia linearly depends on the number of blades. If the average moment of inertia is I_0, then it is obvious that the propeller with N blades has the total moment of inertia I, which equals to:

$$I = NI_0. \tag{5}$$

If, in addition, we start from the assumption that the strength of the interaction depends on the size of the contact surface with the environment, then it can be concluded that the strength of the interaction also linearly depends on the number of blades, so that the damping factor can be written as

$$\gamma = N\gamma_0, \tag{6}$$

where γ_0 is the damping factor in the case $N = 1$ [4].The described dependence of the moment of inertia and the damping factor on the size, i.e. the number of molecular propeller blades, is not included in the standard model of quantum Brownian motion [3], so this model can be considered as an extension of the standard model.

3. The results

The basic method used in this paper to examine dynamic stability is to consider dynamics of the standard deviations of the angle and angular momentum of the rotator, extended by considering dependence of the standard deviations on the number of blades. The obtained results are shown in Figures 1 - 8, where dependence of the standard deviations on time and the number of propeller blades is shown graphically. For convenience and better visibility, in Figures 1 - 3 we present the analytically obtained results for the dimensionless quantities, $\sigma_\varphi, \sigma_L \equiv \Delta\hat{L}/I_0\gamma_0$ for the standard deviations of the angle and the angular momentum observables, and the scaled time $\tau = \gamma_0 t$, where t is time [4]; the surfaces presenting the corresponding classical cases are below the quantum-mechanical counterparts.

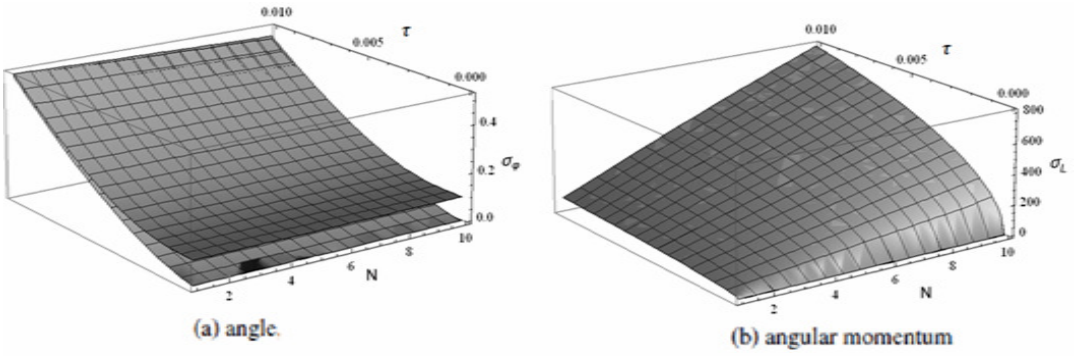

Figure 1. Free rotator, underdamped regime.

Based on the results for the free rotator, it can be concluded that the transition from quantum to classical dynamics for both the angle and angular momentum of molecular propellers is very fast, and it can be noticed that this transition is somewhat faster in the case of angular momentum. For short time intervals, the dynamics of the molecular rotator is subject to the significant quantum corrections, which decrease rapidly with the passage of time, so that it can be said that the quantum domain of the rotator behavior is a short time interval. Quantum corrections also decrease with the increase in the number of molecular propeller blades, i.e. they are smaller for larger molecular propellers. As the number of propeller blades increases, the standard angle deviation decreases while the standard angular momentum deviation increases. It can be said that larger propellers have better angle stability, while smaller propellers have better angular momentum stability. In addition, it is observed that with increasing time, both the standard deviation of the angle and the standard deviation of the angular momentum increase, that is, the stability of molecular propellers decreases. The changes in the standard deviations of the angular momentum over time are significantly larger than the changes in the standard deviations of the angle [4].

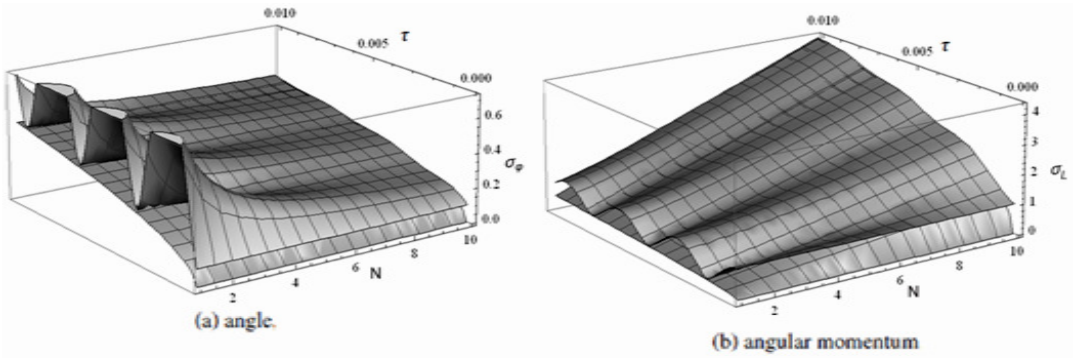

Figure 2. Harmonic rotator, underdamped regime.

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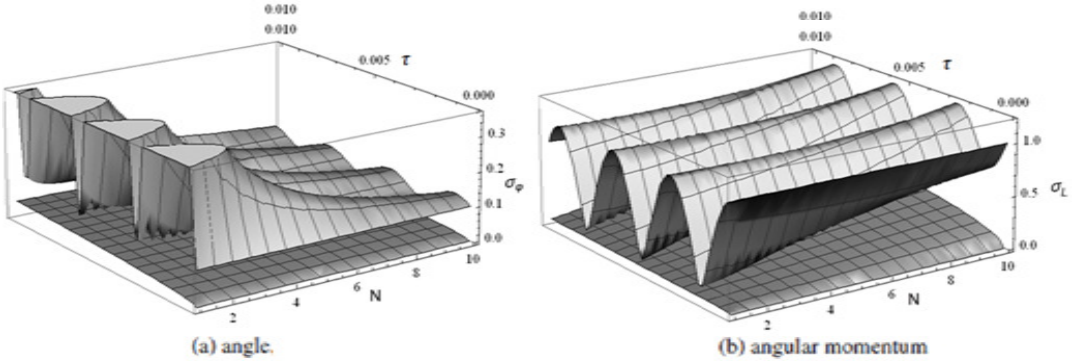

Figure 3. Harmonic rotator, non - underdamped regime.

In the case of a harmonic rotator, the decrease in the standard deviation of the angle with the increase in the number of molecular propeller blades is more pronounced due to the presence of quantum corrections, which significantly decrease with the increase in the number of blades. The standard deviation of the angle is of the same order of magnitude as in the case of a free rotator, while the changes in the standard deviation of the angular momentum are significantly smaller in the case of the harmonic rotator than in the case of a free rotator. The transition from quantum to classical behavior is slower here than in the case of a free rotator. Comparing results for the free and harmonic rotator, it can be concluded that the presence of an external harmonic field leads to better stability of molecular propellers, which means that the use of an external harmonic field can improve controllability of the molecular propellers.

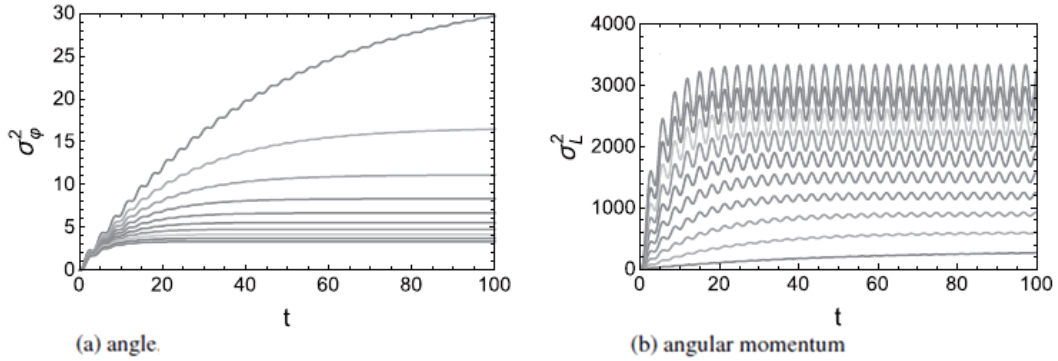

Figure 4. Underdamped regime for rotator in cubic potential, $\gamma_0 = 0.011$, $k_B T = 100$.

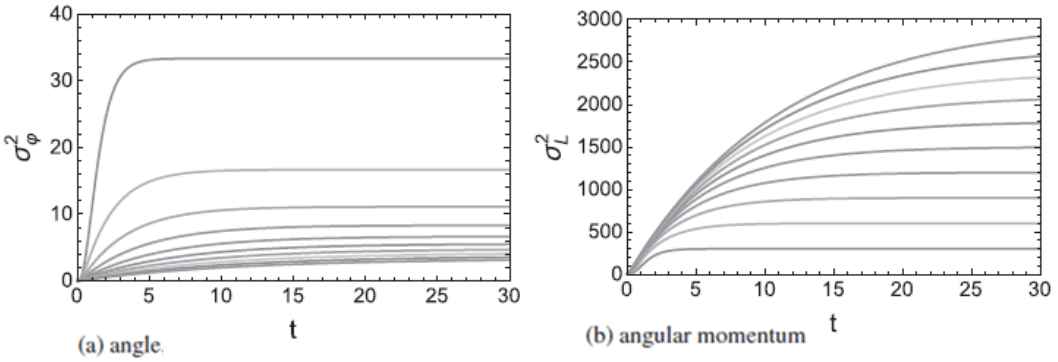

Figure 5. Underdamped regime for rotator in cubic potential, $\gamma_0 = 1.1$, $k_B T = 100$.

The presence of a small cubic term (proportional to the constant b in equation (4)) in the external potential affects the appearance of significant differences in relation to the case of the harmonic potential, especially in the case of the medium and low temperatures. The numerically obtained results are presented in Figures 4-8. In order to reduce numerical errors, the squares of the standard deviations are calculated and presented in the non-scaled time t [5]. At high temperatures, the standard deviations of the angle and angular momentum increase with time. The standard deviation of the angle decreases, while the standard deviation of the angular momentum increases with increasing number of blades, as in the case of a purely harmonic rotator. In the case of low temperatures and large damping factor, which is shown in Figure 6, the standard deviation of the angle decreases with increasing time (which is certainly an unexpected and interesting result), whereby initially the decrease is very intense and fast, while with the passage of time it becomes slower. Interestingly, dependence of the angle standard deviation on the number of blades is not monotonic – there is a minimum $(\sigma_\varphi)_{min}$ for certain values of the number of blades ($N = 3,\ N = 4,\ N = 5$). The standard deviation of the angular momentum decreases very rapidly with time initially, with local minima and maxima within short initial time intervals. In the case of higher values of *N*, a further increase in the standard deviation of angular momentum with the passage of time is noticeable, while this increase in the

case of lower values of N is negligible. The standard deviation of the angular momentum increases noticeably with the increase in the number of blades; this behavior is presented in Figure 6.

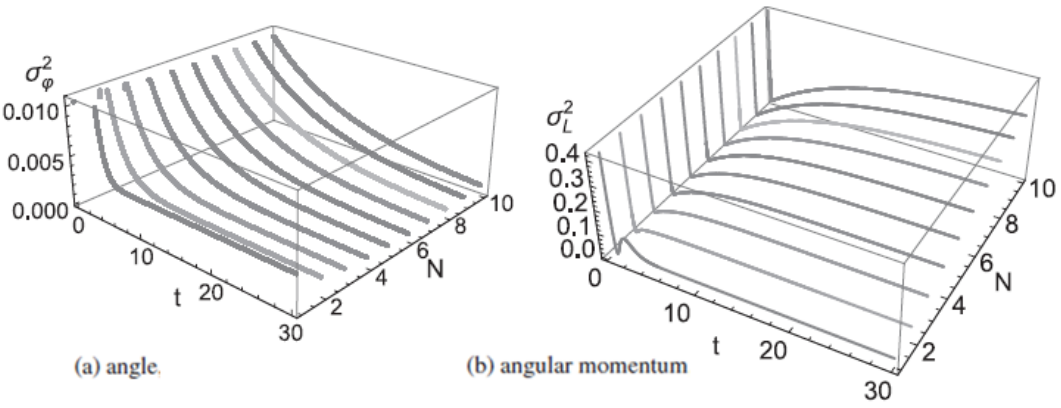

Figure 6. Non - underdamped regime for the cubic potential, $\gamma_0 = 1.1$, $k_B T = 0.01$.

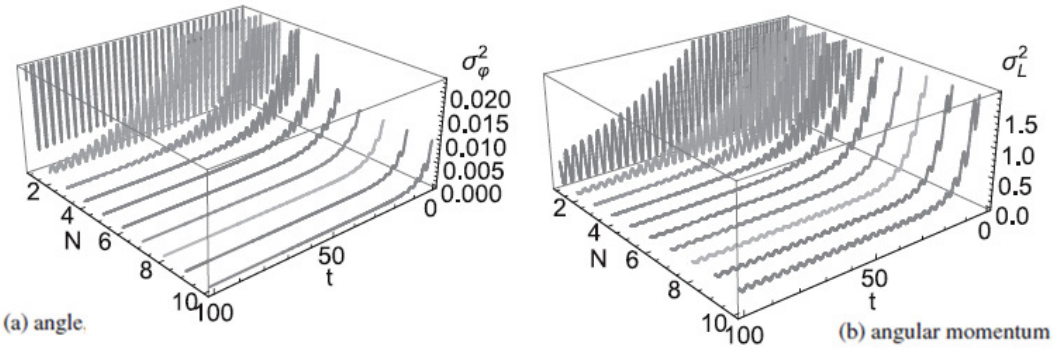

Figure 7. Non - underdamped regime for the cubic potential, $\gamma_0 = 0.011$, $k_B T = 0.01$.

In the case of low temperatures and a small damping factor, which is shown in Figure 7, an unexpected decrease in the standard deviations of the angle and angular momentum with the passage of time is also observed. On the other hand, also in this case the standard deviation of the angle decreases with the increase in the number of blades, while the standard deviation of angular momentum can be said to increase with the increase in the number of blades only if short time intervals are considered. As time increases, the standard deviations of the angular momentum for larger values of N decrease rapidly, while for smaller values of N, oscillations with the amplitudes that more slowly decrease, are noticeable. The decrease in the amplitude of oscillations of the standard deviations is not the same for all values of N. For shorter time intervals, the smallest oscillations of the standard deviations are for $N = 7,\ N = 8$ for both the angle and the angular momentum, while the smallest oscillations of the standard deviations of angular momentum for longer time intervals are for $N = 3,\ N = 4$.

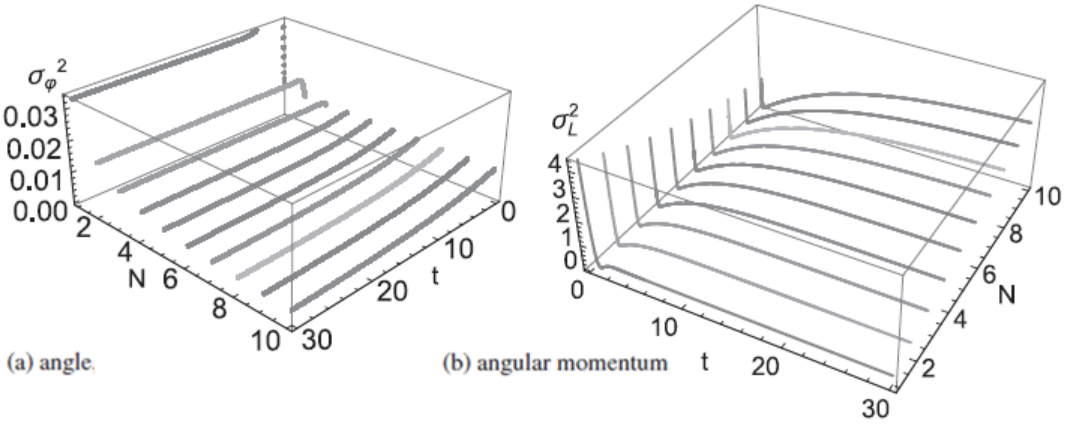

Figure 8. Non - underdamped regime for the cubic potential $\gamma_0 = 1.1$, $k_B T = 0.1$.

In the case of the medium temperatures, as shown in Figure 8, saturation of the time-change of the angle and angular momentum standard deviations can be observed, i.e. it can be said that after some time the standard deviations stop changing with time, while they oscillate with very small amplitudes around some equilibrium values that change negligibly with increasing time. The described saturation of the standard deviations in a way represents a transition between the two previously considered cases, the case of high temperatures, for which there is a constant increase in standard deviation with the passage of time, and the case of low temperatures, for which there is a constant decrease in standard deviations with the passage of time.

The second method of dynamic stability analysis to be presented is based on the so-called "first passage time (FPT)" method, which regards the minimum time, tFPT, needed for a system to cross a threshold value for the variable of interest. The shorter the tFPT, the faster the transition from the initial state and hence the less stable the system. The process of transferring the method of finding the first passage time from the context of classical physics to the context of quantum theory is not unambiguous primarily because, in quantum theory, there is no notion of trajectory which is the basic notion of the classical first passage time method. The method to be presented is the so-called, "the quantum first passage time" and is defined as the minimum time for which the mean value of the angle $\langle\hat{\varphi}\rangle$ reaches a predetermined value $\hat{\varphi}_{th}$ for the selected initial value $\hat{\varphi}_0$. For each selected initial value $\hat{\varphi}_0$ and the corresponding limit value $\hat{\varphi}_{th}$ of the observable angle, the quantum first passage time, t_{QFPT}, is calculated numerically as the minimum time required for the transition $\hat{\varphi}_0 \rightarrow \hat{\varphi}_{th}$. When examining dynamic stability with this method, it is assumed that the longer the quantum first passage time, the more stable the molecular propeller is, observing dependence of the quantum first passage time on the number of blades for different values of the damping factors and the ambient temperature.The results obtained by this method for the non-harmonic rotator confirm and complement the results obtained through the analysis of standard deviations [5].The two methods used for testing the dynamic stability of a weakly unharmonic rotator complement each other in a certain sense. The method of finding the quantum first passage time proved to be suitable for the

analysis of dynamics in shorter time intervals, where t_{QFPT} shows a numerically relevant dependence only on the damping factor and the size of the molecular propeller. The standard deviations for both the angle and angular momentum exhibit strong dependence on a number of parameters for both shorter and longer time intervals – to be presented in the next section of this paper.

4. Discussion and Conclusion

Analysis of the dynamics of molecular propellers presented in this paper demonstrates the presence of non-negligible quantum corrections, especially in regard of short time intervals. Due to the interaction with the environment, the quantum characteristics become gradually reduced to the classical counterparts, in agreement with the basic quantum decoherence theory. A detailed analysis of the high moment of inertia, which is also called the decoherence limit, due to the dominant influence of the decoherence member in the CL master equation, leads to the conclusion, that quantum decoherence is not the dominant process in the transition from quantum to classical behavior. This interesting and unexpected result indicates the need for additional analysis and interpretation, which could be the goal of some future research. In this context, the question can be asked: is the model of molecular propellers special for some reason, an exception, or perhaps it indicates some general views, which may lead to a revision of the existing knowledge regarding the problem of the boundary area between the quantum and classical domains?

The observed non-monotonic dependence of the standard deviation of the angle on the number of blades and also the decrease in the standard deviations with the passage of time in the case of weakly unharmonic rotator are unexpected and interesting results both from the point of view of potential application and from the point of view of theoretical considerations, because it suggests that the "size" of a physical system is not such a simple term in a quantum / classical context. The role of the size of the propellers cannot be reduced to the more-or-less pure inertial effects, which are widely known and expected in the classical physical context [4,5].

A detailed analysis of the impact of different parameters on the dynamic stability of molecular propellers leads to the conclusion, that there are no simple rules or guidelines that would provide the required level of dynamic stability of molecular propellers. To this end, instead of some simple rules, it is necessary to apply a combination of the different stability criteria [5]:

A. The choice of the observable to be acted on

It is easier to achieve controllability of the angle for a free and harmonic rotator in the case of molecular propellers with a larger number of blades, while it is easier to achieve controllability of the angular momentum in the case of molecular propellers with a smaller number of blades. In the case of weakly unharmonic rotator, controllability of the angle is easiest to achieve in the case of a large damping coefficient and low temperatures, and for relatively longer time intervals, when the choice of $N \in \{4, 5, 6\}$ should be made especially if the relatively small magnitude of change of the standard deviation is required—cf. Figure 6(a).

However, if it is preferable to quickly perform certain actions on the system [cf. criterion(E)] after the system initialization, then manipulation of the angular momentum may be a preferred choice when $N \in \{3, 4, 5\}$—cf. Figure 6(b).

B. The parameter regime

In the case of a free and harmonic rotator, it was noticed that increase in the damping factor increases stability of the angle while simultaneously decreasing stability of the angular momentum; on the other hand, increase in temperature implies decrease in stability of both the angle and the angular momentum observables. In the case of a weakly unharmonic rotator even for the same ratio of $\frac{\gamma}{\omega}$, a large difference in dynamic characteristics can be observed. Generally, the small temperature of the environment provides better stability; nevertheless, there are certain exceptions when it comes to short-term behavior [cf. criteria (D) and (E) below], which is significant for the protocols immediately following the system initialization.

C. The magnitude of change of the standard deviations

The magnitude of change in the standard deviation of the angle is smaller than the magnitude of change in the standard deviation of the angular momentum, both in the case of the free and harmonic rotator. In the case of a weakly unharmonic rotator, the magnitude for the angle is smaller, except for $N = 1$ (cf., e.g., Figure 5). When it comes to the amplitude of oscillation, a completely different conclusion is reached. Then a non-monotonic dependence on the number $N$of the blades can be observed–cf. Figures 6,7 and 8.

D. The short- versus the-long time behavior

The conditions for achieving the best possible controllability of molecular propellers are not the same for short initial and longer time intervals. At short initial time intervals, quantum corrections must also be considered, as well as the fact that the dynamic characteristics differ significantly for different combinations of the parameter values. In the case of a weakly unharmonic rotator, the short-time behavior is in strong conjunction with the above items (A) and (B) and may prefer the relatively high temperature – compare, e.g., Figures 5 and 6. The long-time behavior generally exhibits saturation of the standard deviations and, in this sense, a more reliable prediction. The choice of the time scale for the system manipulation cannot be made without a reference to all the other criteria, notably the criterion (E). Additionally, for the longer time intervals, the nonmonotonic dependence of the standard deviation of the angle on N is observed—see Figure 6.

E. The rate of the external actions

External actions that are not included in the master equation are likely to increase (and possibly accumulate) standard deviations. As a result, many quick actions performed in a short time interval may result in an uncontrollable increase in the standard deviation(s) when compared to a small number of longer lasting actions performed in the same time interval. Thus,

usefulness of the quick versus the slow actions is strongly related to the above criteria, particularly to the criterion (D).

The possible combinations of the presented criteria A-E essentially require a procedure that is along the lines of the optimization procedures in engineering [5].

Acknowledgements

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