Quantum tunneling and information entropy in a double square well potential: The ammonia molecule

S.T. Tserkis *, Ch.C. Moustakidis, S.E. Massen, C.P. Panos

Department of Theoretical Physics, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece

A B S T R A C T

We study the implications of quantum tunneling on information entropy measures (Shannon and Fisher), disequilibrium and LMC complexity in a Double Square Well Potential (DSWP), using the ammonia molecule as a test bed. We also apply a similar analysis to the Infinite Square Well Potential (ISWP) in order to compare the corresponding results with a system where tunneling is absent. In particular, we show that contrary to the Heisenberg uncertainty product, information-theoretic tools provide a more sensitive analysis and manage to differentiate DSWP from ISWP case, formulating an empirical criterion whether the tunneling effect is present or not.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Classically if a particle is located in one of the wells of a DSWP and does not have sufficient energy to surmount the barrier in the potential, it will be forever confined to that well. Quantum mechanics shows that due to the wave-like nature of the particle, after a certain length of time, there is a non-zero probability that it will be located in the other well. It is therefore quantum mechanically possible for a particle to pass through a barrier that it cannot classically overcome. This phenomenon is known as quantum tunneling effect.

The quantum tunneling results in the splitting of the low-lying energy levels which occur in pairs with slightly different energy values. The transition frequency between the energy levels of each pair is associated with the emission or absorption of electromagnetic radiation. Particularly in the ammonia molecule this transition frequency for the ground-state has been measured at about 24 GHz [1–3]. This phenomenon, namely the inversion spectrum of the ammonia molecule, has been observed through infrared spectroscopy and plays a fundamental role in the principle of operation of the ammonia MASER [4]. Although inversion effect occurs in other molecules as well (PH_3, AsH_3, NH_2CN) [3,5], NH_3 provides a tractable vibrational system for experimental observation and exploitation, since inversion frequency falls in the microwave region.

Until recently, oscillation of probability density in position space $\rho(x, t)$ between the wells has been the usual way to approach the quantum tunneling phenomenon and consequently the inversion spectrum. Heisenberg uncertainty product reflects this phenomenon, but information entropy offers a more sensitive approach to study a particle moving in a non-classical way through the barrier.

Information-theoretic tools, initially applied to communication systems, have been employed extensively to investigate various classical and quantum systems e.g. in physics [6], chemistry [7,8], biology [9] and many other scientific branches as well. Specifically, the well-known information measures defined by Shannon [10] and Fisher [11], have been applied with considerable success in quantum systems e.g. atoms [12,13]. Shannon information entropy has been correlated fairly well with experimental data for atomic ionization potentials and dipole polarizabilities [14]. A comprehensive account of applications to molecules can be found in [15] and [16]. Another example is an information-theoretic treatment of a molecule (π-system) described in [8].

To begin with, one needs a probabilistic treatment of a system, which in fact is especially suitable and relevant for quantum systems, and then use the corresponding probability densities, $\rho(\mathbf{r})$ in position space and $n(\mathbf{k})$ in momentum space as input to the definitions of Shannon information entropy and Fisher information. Thus, one proceeds to the calculation of the information content of the system and investigate its related properties. An additional merit of the probabilistic treatment is that one can calculate quantitatively, in a systematic manner, a measure of complexity of the quantum system, the so-called LMC statistical complexity [17]. The LMC complexity of the H_2^+ ion was studied using a simple wavefunction of Coulson type, leading to a promising relation of complexity with chemical bonding [18]. Atomic complexity has been

* Corresponding author.
E-mail address: stserkis@physics.auth.gr (S.T. Tserkis).

calculated for the first time in the literature in [19], where another definition of complexity was employed, namely the SDL measure [20]. Last but not least, calculations of molecular information entropies were carried out in [21,22].

In the present paper we apply the above methods in order to study the ammonia molecule as a test bed, and in particular to assess the effect of tunneling on the Shannon information entropy, the Fisher information and the LMC complexity, together with Heisenberg uncertainty product. We employ a simple model for the ammonia molecule, i.e. the Double Square Well Potential (DSWP), which captures its essential properties required for a probabilistic treatment via the Schrödinger Equation.

This paper is organized as follows. In Section 2 we define the relevant information measures and present the intrinsic relation among them. In Sections 3 and 4 we derive the time-dependent wavefunction for the ammonia molecule (DSWP) and for the Infinite Square Well Potential respectively, in order to compare the corresponding results of the DSWP with a system, where quantum tunneling is absent. In Section 5 we discuss our results, while the conclusions of the analysis are drawn in Section 6. Finally we illustrate the obtained figures in a separate section at the end of the paper.

2. Information measures

The Shannon information entropy [10,23] for a discrete probability distribution p_i with N accessible states, is defined as

$$S = -\sum_{i=1}^{N} p_i \log p_i, \tag{1}$$

while for a continuous probability density $f(x)$ is usually called "differential entropy" [23] and is defined as

$$S = -\int f(x) \log f(x)\, dx. \tag{2}$$

In quantum mechanics, for a continuous distribution representing the probability density in position space $\rho(\mathbf{r})$, takes the form

$$S_r = -\int \rho(\mathbf{r}) \ln \rho(\mathbf{r})\, d\mathbf{r}, \tag{3}$$

and the corresponding momentum space entropy S_k is given by

$$S_k = -\int n(\mathbf{k}) \ln n(\mathbf{k})\, d\mathbf{k}, \tag{4}$$

where $n(\mathbf{k})$ denotes the momentum probability density [24]. The densities $\rho(\mathbf{r})$ and $n(\mathbf{k})$ are respectively normalized to one. The information entropy sum in conjugate spaces $S_T = S_r + S_k$, contains the net information of the system and is typically measured in nats. Individual entropies S_r and S_k depend on the units used to measure r and k respectively, but their sum S_T does not, i.e. it is invariant to uniform scaling of coordinates.

The net Shannon information entropy, in D-dimensions, obeys the following lower bound, also known as the entropic uncertainty relation (EUR)

$$S_T = S_r + S_k \geqslant D(1 + \ln \pi), \tag{5}$$

which represents a stronger version of the Heisenberg uncertainty principle of quantum mechanics, in the sense that the EUR leads to Heisenberg relation, while the inverse is not true [6].

Shannon's information entropy ("uncertainty") provides a global measure of smoothness [25] and reflects the indeterminacy ("spread") of a distribution, since a highly localized $\rho(\mathbf{r})$ is associated with a diffuse $n(\mathbf{k})$, leading to low S_r and high S_k and vice-versa. In other words, Shannon information entropy measures the average amount of the information received, when this uncertainty is removed by an appropriate "localization" experiment [26].

The Fisher information measure I_θ [11,25,27], also called the "intrinsic accuracy", corresponding to a family of probability densities $f(x; \theta)$ and depending on a parameter θ is given by

$$I_\theta = \int \frac{1}{f(x; \theta)} \left(\frac{\partial f(x; \theta)}{\partial \theta} \right)^2 dx, \tag{6}$$

while for a discrete distribution [25,28] is defined as

$$I = \sum_{i=1}^{N} \frac{(p_{i+1} - p_i)^2}{p_i}. \tag{7}$$

In quantum mechanics, Fisher information in position space takes the form

$$I_r = \int \frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})}\, d\mathbf{r}, \tag{8}$$

and the corresponding momentum space measure is given by

$$I_k = \int \frac{|\nabla n(\mathbf{k})|^2}{n(\mathbf{k})}\, d\mathbf{k}. \tag{9}$$

The individual Fisher measures are bounded through the Cramer–Rao inequality according to $I_r \geqslant \frac{1}{V_r}$ and $I_k \geqslant \frac{1}{V_k}$, where V_r and V_k denote the corresponding spatial and momentum variances respectively [29,30].

In contrast to Shannon's information entropy which provides a global way of characterizing "uncertainty", Fisher's information provides a local measure of smoothness and reflects the "narrowness" of the probability distribution [25,26]. Furthermore, Fisher's information is strongly sensitive to the local oscillatory character of probability density, due to the fact that it depends on its gradient [27].

In position space, the Fisher information measures the "sharpness" of probability density, i.e. a strongly localized probability density gives rise to a larger value of Fisher information and vice-versa. In this sense, Fisher information is complementary to Shannon information entropy and their reciprocal relation is, in fact, utilized in this work.

If either the momentum space wavefunction $\phi(k)$ or the position space wavefunction $\psi(x)$ is real, it has been shown [27] that the net Fisher information ($I_T = I_r I_k$), in D-dimensions, obeys the following lower bound

$$I_T = I_r I_k \geqslant 4D^2. \tag{10}$$

The lower bounds of both Shannon sum ($S_r + S_k$) and Fisher product ($I_r I_k$) get saturated for the Gaussian distributions [25].

Fisher's information is also intimately related to the Shannon information entropy via de Bruijn identity [23,30]

$$\frac{\partial}{\partial t} S(x + \sqrt{t}z) \Big|_{t=0} = \frac{1}{2} I(x), \tag{11}$$

where x is a random variable with a finite variance with a density $f(x)$, and z an independent normally distributed random variable with zero mean and unit variance.

In a statistical analysis we are usually interested in knowing how far the system deviates from equilibrium. For a discrete distribution with N accessible states, the quantity

$$D = \sum_{i=1}^{N} \left(p_i - \frac{1}{N} \right)^2, \tag{12}$$

is called disequilibrium, and represents the distance from equilibrium [17]. For the continuous case disequilibrium is defined as