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Reconsidering harmonic and anharmonic coherent states: Partial differential equations approach

Mohamad Toutounji

College of Science, Department of Chemistry, UAE University, P.O. Box 15551, Al-Ain, United Arab Emirates

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ABSTRACT

This article presents a new approach to dealing with time dependent quantities such as autocorrelation function of harmonic and anharmonic systems using coherent states and partial differential equations. The approach that is normally used to evaluate dynamical quantities involves formidable operator algebra. That operator algebra becomes insurmountable when employing Morse oscillator coherent states. This problem becomes even more complicated in case of Morse oscillator as it tends to exhibit divergent dynamics. This approach employs linear partial differential equations, some of which may be solved exactly and analytically, thereby avoiding the cumbersome noncommutative algebra required to manipulate coherent states of Morse oscillator. Additionally, the arising integrals while using the herein presented method feature stability and high numerical efficiency. The correctness, applicability, and utility of the above approach are tested by reproducing the partition and optical autocorrelation function of the harmonic oscillator. A closed-form expression for the equilibrium canonical partition function of the Morse oscillator is derived using its coherent states and partial differential equations. Also, a nonequilibrium autocorrelation function expression for weak electron–phonon coupling in condensed systems is derived for displaced Morse oscillator in electronic state. Finally, the utility of the method is demonstrated through further simplifying the Morse oscillator partition function or autocorrelation function expressions reported by other researchers in unevaluated form of second-order derivative exponential. Comparison with exact dynamics shows identical results.

E-mail address: Mtoutounji@uaeu.ac.ae.

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1. Introduction

Probing time development of anharmonic systems for acquiring dynamical and structural information can be challenging, especially when Morse potential is employed for accounting for the anharmonic character of the system of interest. Besides the difficult algebraic nature of Morse potential, Morse oscillator tends to display divergent dynamics [1–5]. Additionally, dynamical calculations that involve utilizing Morse oscillator eigenfunctions suffer from numerical instabilities and convergence issues. Furthermore, essential singularity issues crop up in the classical limit upon using Morse Hamiltonian. A long standing problem in Morse oscillator dynamics or statistical mechanics has been the divergence that arise upon evaluating average values and time correlation functions classically [4] or quantum mechanically [1,5]. This particular problem has been elucidated by Toutounji in detail [2–4].

The above difficulties associated with using Morse oscillator have always motivated research groups to come up with techniques to surmount those difficulties. Very recently, Toutounji [6] has used Morse coherent states as an alternative to using Morse oscillator eigenstate representation or its corresponding propagator. Coherent states (harmonic or anharmonic) can be algebraically very demanding. The difficulty traces back to the noncommuting operators involved in coherent states manipulation. Besides, unfamiliar expressions involving operator algebra which often lead to infinite series might crop up, while using coherent states, that is not easily summable to a finite value [7,8].

The main focus of this article is to present a new approach for evaluating time-dependent variables that are essential components to spectroscopy and quantum dynamics, e.g. linear/nonlinear dipole moment time/frequency correlation function, position correlation function, quantum solvation, wavepacket dynamics, scattering, etc. These quantities require time evolution operator acting on the state function of the system of interest. Morse oscillator has been well utilized in modeling anharmonic molecular vibrations for which the reason it will be used herein as the system of interest for probing anharmonic nuclear dynamics. Different groups have expended efforts on developing anharmonic ladder operators for the purpose of constructing of Morse oscillator coherent states [9–15], but not much on their utility and the corresponding operations of its coherent states in dynamics. For example, Popov and coworkers, and others, have reported important work on Morse oscillator coherent states, however their work was missing utility and operational properties of Morse coherent states [9–11].

The motivation for our work is the recent article by Popov et al. [15] where their results were reported in terms of sums and exponential derivatives. It turns out that employing partial differential equations approach can help eliminate the sums and derivatives and recast the results in a closed form. This approach has made us realize that manipulating coherent states may be reconsidered using the aforementioned approach, leading to more manageable results, including harmonic coherent states which will be used here for ratifying and illustrative purposes. However, our main focus here will be solving problems related to Morse coherent states and the associated spectroscopy and dynamics such as evaluating time-correlation functions. This method has come to our attention during the course of the work that had led to the work in Ref. [6]. Toutounji [8] had used a system of first-order linear ordinary differential equations to solve noncommutative algebra related problems, whereby linear and quadratic electron–phonon coupling in condensed phase systems was treated.

Recently, Popov et al. [10,11,15] and Lemus [16] have done remarkable work on the algebraic structure of Morse coherent states and dynamical related issues. Most notable work in [15] is Morse thermal states which we intend to explore using the herein presented approach. In this article, the equilibrium canonical partition function and non-equilibrium autocorrelation function of harmonic oscillator are reproduced analytically using partial differential equations approach instead of manipulating harmonic coherent states algebraically to ratify the correctness and applicability of the presented approach. Similarly, the corresponding functions of Morse oscillator are derived using the same differential approach, rather than the algebraic one.

2. Harmonic oscillator thermal states and quantum dynamics

Although the results provided in this section are well known in the literature, they are reproduced for illustrative and ratifying purposes of the approach presented herein. While the first part of this