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Non-Gaussian wave packet dynamics in anharmonic potential: Cumulant expansion treatment

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ABSTRACT

This manuscript utilizes cumulant expansion as an alternative algebraic approach to evaluating integrals and solving a system of nonlinear differential equations for probing anharmonic dynamics in condensed phase systems using Morse oscillator. These integrals and differential equations become harder to solve as the anharmonicity of the system goes beyond that of Morse oscillator description. This algebraic approach becomes critically important in case of Morse oscillator as it tends to exhibit divergent dynamics and numerical uncertainties at low temperatures. The autocorrelation function is calculated algebraically and compared to the exact one for they match perfectly. It is also compared to the approximate autocorrelation function using the differential equations technique reported in Toutounji (2014) for weak and strong electron–phonon coupling cases. It is found that the present cumulant method is more efficient, and easier to use, than the exact expression. Deviation between the approximate autocorrelation function and the exact autocorrelation function starts to arise as the electron–phonon coupling strength increases. The autocorrelation function obtained using cumulants identically matches the exact autocorrelation function, thereby surpassing the approach presented in Toutounji (2014). The advantage of the present methodology is its applicability to various types of electron–phonon coupling cases. Additionally, the herein approach only uses algebraic techniques, thereby avoiding both the divergence integral and solving a set of linear first- and second-order partial differential equations as was done in previous work. Model

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calculations are presented to demonstrate the accuracy of the herein work.

1. Introduction

Researchers in physics and chemistry normally probe time dependent observables by assuming a Gaussian wavepacket in the initial state from which they then start probing (propagating) for the harmonic or anharmonic system in question. (If the system is harmonic, then Gaussian treatment is exact.) Initial value representation (IVR) is one popular methodology that tends to use this type of propagation [1–3]. In the framework of Mukamel's theory [4] the alluded-to-Gaussian is called Liouville space generating function (LGF) which is an approximate function for anharmonic systems modeled by Morse oscillator. IVR entails running many trajectories and solving multidimensional integrals, whereas LGF requires solving a system of nonlinear differential equations. Both techniques are semiclassical. While cumulant expansion has been widely used in harmonic systems, to the best of our knowledge, this manuscript is the first work which utilizes cumulant expansion in calculating anharmonic dynamical quantities.

The focus of this article is 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 molecular vibrations for which the reason it will be used herein as the system of interest for probing anharmonic nuclear dynamics. As pointed out earlier, people tend to use IVR and LGF for that purpose, which require running integral techniques and solving a system of nonlinear inhomogeneous differential equations. The cumulant expansion approach being proposed herein is purely algebraic technique whereby evaluating integrals and solving a system of differential equations are avoided. It is noteworthy that while the integrals and differential equations that arise in case of harmonic systems are straightforward, this is not the case with anharmonic dynamics as many challenges may arise, especially in case of using anharmonic oscillator [5]. As such, using cumulants circumvent all these challenging issues that crop up when using an anharmonic oscillator such as Morse oscillator.

This manuscript briefly proposes utilizing cumulant expansion in case of employing Morse oscillator to probe anharmonic nuclear dynamics as this approach lends itself more readily than the above cited techniques, including those of the author which require solving partial differential equations (PDE) [6]. That is, it is more straightforward than the above approaches; it further avoids dealing with difficult issues such as divergence and solving PDEs that may not easily be solved. Besides the just-said-advantages, the applicability of this algebraic approach is more expansive than other approaches with respect to the strength of the electron–phonon coupling cases, whereas the PDE approach presented in Ref. [6] is only good for weak electron–phonon coupling cases. The dynamical quantity to be calculated here is the autocorrelation function whose absolute value square leads to survival probability. This cumulant approach is hoped to set the stage for using it in other anharmonic oscillators.

This paper is organized as follows. Section 2 starts with two adiabatic surfaces where the initial ground state and the final (excited) are, respectively, represented by Morse potential and displaced Morse potential in order to evaluate the Morse oscillator autocorrelation function of the electronic transition between the two surfaces using cumulant expansion whereby only algebra is utilized, precluding any differential and integral techniques. The wavepacket representing the initial state will not be Gaussian as is customarily assumed in case of anharmonic systems. Section 3 provides model calculations of the optical autocorrelation function where the present method is compared to the exact and that produced by the PDE approach. Section 4 concludes that the cumulate expansion method